THE MECHANISM OF FORMATION OF THE MIXED BORON TRIHALIDE ADDUCTS OF TRIMETHYLAMINE

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ABSTRACT

Boron trihalide and mixed boron trihalide adducts of trimethylamine have been prepared, and characterized by proton and fluorine N.M.R. spectroscopy. The acceptor power of the boron trihalides was seen to increase in the order $BF_3 < BCl_3 < BBr_3 < BI_3$, corroborating previous evidence. The mixed boron trihalides had intermediate Lewis acidities.

Solution reactions between adducts and free boron trihalides rapidly led to the formation of mixed adducts when the free boron trihalide is a stronger Lewis acid than that in the adduct. A slower reaction is observed when the free BX_3 is a weaker Lewis acid than that complexed.

The mechanism of halogen exchange leading to the mixed $(CH_3)_3NBX_3$ adducts was investigated. ^{10}B labelling experiments precluded B-N bond rupture as a possible mechanism in solution; results are discussed in terms of halogen-bridged intermediates. Pre-ionization may be important for some systems. At higher temperatures, during gas phase reactions, B-N coordinate bond rupture may be the initial step of reaction.

Two mixed adducts, namely $(CH_3)_3NBClBr_2$ and $(CH_3)_3NBHClBr$ were prepared and characterized by Mass Spectrometry.

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INTRODUCTION

A. ADDITION COMPOUNDS OF LEWIS ACIDS AND BASES

i) The Nature of the Donor-Acceptor Bond

There is a considerable difference of opinion over the nature of the Donor-Acceptor bond. Mulliken (1) argued that the predominant contribution to the energies of formation and dipole moments of D-A complexes arose from charge transfer interactions. This charge transfer process is viewed as occurring between an occupied orbital in the donor molecule and an unoccupied molecular orbital in the acceptor molecule (2).

The extent to which classical electrostatic forces, including coulombic (e.g. dipole-dipole) and polarization (e.g. dipole induced dipole) attractive forces, contribute to the energy of D-A bonds has been examined by other workers (3-7). Hanna (3) has shown that the stability of the benzene-iodine complex can be explained by considering the contributions of both the charge transfer and quadrupole induced dipole forces. The observed dipole moment must be due, in part, to the polarization forces, a

possibility that had previously been neglected by Mulliken.

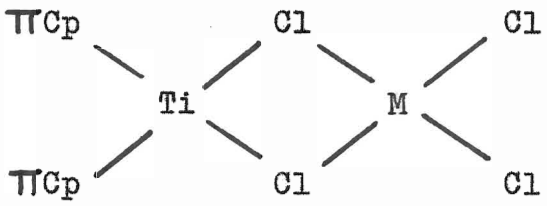
A recent review (2) suggests the probability that the formation of Donor-Acceptor bonds involves use of all types of force, both classical electrostatic and charge transfer, and that properties attributable to such bonds are dependent on the size and importance of a particular contribution. Later work by Mulliken also concludes that electrostatic forces may make significant contributions to bond strength in weak adducts (8) while charge transfer effects predominate for stronger complexes (9).

The number of books (10-13) and reviews (2, 14-25) now available reflects the increasing interest in this field of study. Some of the experimental techniques used in measuring Donor-Acceptor interaction are dealt with in articles by Andrews (14) and Stone (23); these include solubility, conductance and vapour pressure measurements, calorimetry and estimations of the dipole moments (2). More recently, spectrophotometry (26, 27), N.M.R. (28-30), mass spectrometry (31) and X-ray crystallography (32) have found increasing use in the study of these problems.

ii) Donor-Acceptor Complexes

Many molecular addition compounds have been described for Group IIIA, the majority containing boron.

Complexes of Group IIIA chlorides with di-π-cyclopentadienyltitanium have the structure:-



M = B, Al, Ga, In

The interaction of the titanium III unpaired electron with the acceptor nucleus has permitted use of electron paramagnetic resonance spectroscopy to estimate (33) the relative Lewis acid strength of the Group IIIA metal chlorides. The acid strength has been found to decrease in the order Ga > B > Al > In. The unexpectedly high relative acidity of gallium trichloride has been explained in terms of the effective nuclear charge which increases considerably on going from aluminium to gallium. This is offset by the increase in size which diminishes acceptor capacity. A d-d overlap between gallium and titanium may also influence the Lewis acidity by allowing the metals to approach more closely. Such an influence has already been postulated for Ti-Ti bonds in $Cp_2TiCl_2TiCp_2$ (34). If boron trichloride is assigned an

arbitrary value of 100, then this order may be compared (Table 1) to a similar series obtained by Deters et al (35) from proton N.M.R. measurements of the same acids toward tetrahydrofuran.

TABLE 1 Relative Lewis Acidity in MCl_3

M	From E.P.R. (33)	From N.M.R. (35)
^{69}Ga	150	-
^{71}Ga	150	-
^{11}B	100	100
^{27}Al	86	81
^{115}In	53	64

E.P.R. studies were also used (36) to confirm the relative Lewis acidities of the boron trihalides; complexes of the latter with stable nitroxide free radicals (R_2NO) were used. The results indicated that the order of acceptor power increased as $BF_3 < BCl_3 \lesssim BBr_3$.

High precision gas-liquid chromatography has been used (37) in a thermodynamic study of complex formation. The equilibrium constants for the interaction between dibutyl tetrachlorophthalate and bases such as furan and pyrrole measured in this way show good agreement with

theoretical predictions and values measured by more conventional techniques.

Coordination complexes of other Group IIIA metals such as indium (38), gallium (39, 40) and thallium (41, 42) have been studied using I.R., Raman and N.M.R. spectroscopy, whilst the chemistry of organoaluminium adducts has been covered by Mole (43-45), his co-workers and others (46-48).

iii) The Boron Trihalides as Lewis Acids

The boron halides are sp^2 hybridized molecules and as such possess an empty 2pz orbital which gives the molecule strong Lewis acid characteristics. The B-X bond is normally shorter than the sum of the covalent radii of boron and the halogen, and the bond lengths decrease in the order BI > BBr > BCl > BF (49).

The different strengths of the Lewis acids on complex formation have been attributed (50) to a) the electronic structure and b) the reorganization energy from compound to compound. The latter term will undoubtedly be influenced by the polar and steric effects of substituents on both the acid and base (51). This was the basis of Brown's "face to face" or F-strain theory (52), which held that steric hindrance would lower the apparent acid or base strength. But the order of donor strength for a series of alkyl substituted pyridines towards the boron

halides was found to decrease as 2-alkyl > 4-alkyl > 3-alkyl > py. (53, 54); the opposite order to that expected from Brown's postulate in which steric interaction between the 2-alkyl group and the boron trihalide would be a maximum. Contrary to this report is a similar study by Fratiello and Schuster (55). They found that the complexing ability of alkyl pyridines decreased in the order 4-Mepy. > 3-Mepy. > py. > 2-Mepy. > 2,6-Mepy.; clearly, good agreement with Brown's theory.

The classically accepted order of acceptor power of the boron trihalides was $BF_3 > BCl_3 > BBr_3 > BI_3$ (56), this order being based on the steric limitations and the electronegativities of the halogens. Much work in the last two decades has indicated that this is not necessarily the case; that the correct order is opposite to that cited above. Some qualitative data has accumulated to support this view. Thus BF_3 does not complex with arsine (58) whereas the BCl_3 (59) and BBr_3 (60) adducts are stable to $0^{\circ}C$; PCl_3 and PBr_3 react with BBr_3, but neither react with BCl_3 and BF_3 (61). Laubengayer and Sears (62) also indicated the correct order of Lewis acidity; they showed the heat of formation of $MeCN.BCl_3$ to be greater than that of $MeCN.BF_3$. The importance of this may not have been recognized, for interest in this area waned and a decade passed before a firm foundation was laid by Brown and

Holmes (57). They measured the molar heat of reaction of BX_3 (X = F, Cl, Br) with nitrobenzene and showed that the Lewis acidity increased in the order $BF_3 < BCl_3 < BBr_3$. The complexation shift of the nitrile group to higher frequency has been used to estimate Lewis acidity (255) although calculations have illustrated some of the difficulties encountered with this technique (256). Other work has also served to confirm that the order is $BF_3 < BCl_3 < BBr_3$ (62, 69, 135, 157, 67, 26).

The trend in Lewis acidity can best be explained by considering $P\pi - P\pi$ bonding (169) in the free boron trihalides and assuming that some survives in the tetrahedral adducts. Drago et al (70) predicted that differences in $P\pi - P\pi$ overlap energies between planar and pyramidal molecules are small and they therefore argue that large amounts of π-bonding survive in the adducts. The degree of π-bonding destroyed probably depends on the strengths of the donor, since donor electrons compete with halogen electrons for occupation of the empty boron orbital.

In BX_3, overlap of the empty 2pz boron orbital with the filled halogen npz is at a maximum when X = fluorine, resulting in a large degree of π-bonding. Steric considerations make similar overlap with chlorine, bromine and iodine progressively less effective. This decreasing order of π-bonding was confirmed by N.M.R.

studies (257) and molecular orbital calculations (169); the latter also showed the reorganisation energy to be in the same order, namely $BF_3 > BCl_3 > BBr_3$. Recently however, the extent of π-back donation has been determined by theoretical studies (228), mass spectral analysis (218) and from measurement of the quadrupole coupling constant in boron (258). These results all supported N.Q.R. data in which the values of the field gradient asymmetry parameter at the halogen atom (259-261) were found to be consistent with a π-bonding order $BI_3 > BBr_3 \simeq BCl_3 > BF_3$. Without contradicting these results, Bassett and Lloyd (219) showed the stabilization energy -- as measured from photoelectron spectra -- to be in the opposite order; thus B-F bonds still contain the greatest π-bonding energy.

The concept of reorganization energy to predict Lewis acidity may only be an acceptable criterion when the formation of adducts is being considered. It has been pointed out (188) that measurements made on adducts after their formation, e.g. dipole moments and I.R. give a similar order of acceptor power to that obtained from heats of formation data. It seems likely, therefore, that this data reflects the relative B-N bond strengths (253). Further evidence for the order of acceptor power has been collected from microwave and X-ray diffraction studies (136, 184). These data show the donor-acceptor bond

length increasing in the order $BI_3 < BBr_3 < BCl_3 < BF_3$.

Dipole moments of trimethylamine and pyridine adducts (69) show that BH_3 is a slightly stronger acid that BF_3. Indeed it has been calculated (164) that if BH_3 existed as a stable monomer it would be a better electron acceptor than BF_3. Other work indicates that the relative strengths vary depending on the base being used. Thus $BF_3 > BH_3$ when dimethyl ether is used (160, 161), while the order is reversed on using trimethylphosphine (162, 163); with trimethylamine the strengths seem about equal (28, 63).

The unusual acceptor power of the BH_3 group may be explained by extending the proposal of Burg et al (262, 263) who suggested that the BH_3 group could release electron density to certain ligandshaving suitable vacant orbitals.

It is possible to regard the behavior of the BH_3 group in an adduct as being similar to a methyl group in organic chemistry (64). The three borane protons may be considered as a pseudo-atom giving rise to a π-orbital which is able to overlap with an empty ligand orbital. Such π-π bonds would strengthen the σ bonds.

B. ADDUCTS OF THE BORON TRIHALIDES

i) Introduction

It is generally accepted that for ligands of similar structure, the BX_3 adducts of Group V donors are more stable towards dissociation than the complexes of Group VI donors. This effect has been rationalized in terms of the increase in nuclear charge in passing from Group V to Group VI. Within a group the stability of the complexes tends to decrease with increasing size of the donor atom leading to the relative order N>P>As and O>S>Se (63). However, there are exceptions to this rule. For example, towards borane, P>N and S>O (64). Indeed, in a comprehensive study of this problem, Young et al (65) concluded that the order of base strength depended on the strength of the σ bond formed between boron and the donor. As the acid becomes stronger there is a greater tendency towards this reversal of base strength.

One system in which the donor characteristics might be explained in terms of electronegativity requirements is that of substituted arsines. The arsine BCl_3 and BBr_3 complexes have been mentioned above; yet $AsCl_3$ and $AsBr_3$ show no basic tendencies whatever (61).

ii) Oxygen Donors

Carbonyl compounds have long been known to

behave as Lewis bases, and their complexes with a variety of electron acceptors have been studied in numerous ways (66). After the acyl oxygen had been established as the donor atom (66), Lappert (26) and Cook (67) used the carbonyl group frequency shifts to measure the relative acceptor properties of a series of Lewis acids towards ethyl acetate and xanthone. Their argument was that complex formation caused perturbation of the C=O bond. The strength of the D-A bond could then be estimated by measuring the changes in the carbonyl stretching force constant which, in turn, could be obtained from the change in the I.R. stretching frequency (26, 68).

The changes in the C=O stretching frequency between the free esters and their complexes are shown in Table 2, and indicate the order of Lewis acidity to be $BBr_3 > BCl_3 > BF_3$. Included in the table, for sake of comparison, are data obtained from systems in which nitrogen is the donor. This data supports the same relative order of Lewis acidity, confirming the views that I.R. is a useful technique for assessing D-A interaction.

A quantitative relationship between the carbonyl shift and the calculated enthalpy of formation was shown to exist by Drago et al (70) who proposed a new model for the energetics of adduct formation. This model, which does not require the concept of reorganization energy,

TABLE 2 Changes in the Carbonyl Stretching Frequency Upon Complexation

Lewis Acid	$\Delta\nu$(C=O) CM^{-1}		Heat of Formation (kcal $mole^{-1}$)	Dipole Moment (Debeye) (69)	
	Ethyl acetate (26)	Xanthone (67)	$py.BX_3$ (57)	$Me_3N.BX_3$	$py.BX_3$
BF_3	119	138	31.7	4.04	5.31
BCl_3	176	229	39.5	5.13	6.52
BBr_3	191	253	44.5	5.57	6.90

attempts to represent the energy of the acid as a function of the electron density transferred to it, and the energy of the base as a function of the electron density removed. Other studies have shown that a similar linear relationship between the enthalpy of adduct formation and the O-H stretching frequency shift exists for phenols (71, 72) and aliphatic alcohols (73, 74).

The question of whether oxygen is the donor atom in amides and urea complexes has been of interest for some time (75). The observation that proton-proton coupling constants across the C-N bond increase, and that slow rotation of the methyl groups about the C-N bond of N, N-dimethylformamide continues with complex formation is consistent with oxygen donation (76, 78). Similarly

two recent reports have conclusively established oxygen to be the donor in dimethyl (79) and tetramethyl (80) ureas, although Greenwood and Robinson (81) suggested nitrogen coordination to be of importance in several other alkyl substituted ureas. Hartman (80) has shown their results to be in error, possibly because their BF_3 was contaminated with HF.

The donor strengths of some para-substituted acetophenones towards BF_3 were estimated by Moodie (82) from measurements of the equilibrium constants for the reaction

$$L + BF_3.OEt_2 \rightleftharpoons LBF_3 + Et_2O$$

where L = $CH_3O.A$, $CH_3.A$, H.A (A = acetophenone)

K equilibrium was found to decrease in the order $CH_3O.A > CH_3.A > H.A$.

A comprehensive study of ketone-BF_3 complexes was carried out by Gates and Mooney (83) who used both I.R. and N.M.R. evidence in an effort to ascertain the relative donor properties of the bases. However, only fluorine-19 N.M.R. and the B-O stretching frequencies were found to be useful in providing an accurate measure of donor strength; the other methods could not be reliably used since the complexation shifts fell into too narrow a range.

Many other studies of oxygen coordination have

been reported. These include investigations of the exchange reactions of complexes of ketones (84, 85), ethers (86, 87), alcohols (88, 89, 90) and water (91); theoretical and experimental measurements of enthalpies of reaction (92-94) and a study (95) of the effect of varying R in RCO_2Et showed some unusual trends in the relative Lewis acidity of the boron halides.

iii) Phosphorus Donors

The study of the chemistry of B-P complexes has been limited mainly to the study of B III and P III; trivalent phosphorus is able to donate a lone pair of electrons, while boron III compounds behave as Lewis acids. The largest single class of these compounds is that of adducts of borane -- or its derivatives -- with phosphine or substituted phosphines.

The relative Lewis acidity of the boron trihalides towards phosphorus III halides is generally the same as that towards other donors; namely, $BF_3 < BCl_3 < BBr_3 < BI_3$. The order of basic strength of the phosphorus halides is $PF_3 < PCl_3 < PBr_3 < PI_3$, the order being governed by the electronegativity of the substituents (96) provided steric requirements are not important. Thus 1 : 1 complexes are formed only between the strongest acids and bases and generally adducts of PE_3 with the boron trihalides are not

known (49, 97-99). Similarly, PCl_3 will react only with BBr_3 and BI_3 (61, 100-102), contrary to previous reports which outlined the preparation of $PCl_3.BCl_3$ (59) and $PCl_3.BF_3$ (103). With $PCl_3.BBr_3$ and $PCl_3.BI_3$ cross halogenation occurs (100) slowly to form PBr_3 and PI_3 respectively, and boron trichloride, indicating the reluctance of BCl_3 to form adducts with halogeno-phosphines. The strongest donors, PBr_3 and PI_3 readily complex with BI_3 and BBr_3 (97, 100, 104-106) but not with BF_3 and BCl_3 (97, 100).

That the phosphorus trihalides are even weaker bases than phosphine is clear to see since the majority of phosphine boron halide complexes are well established (107-110). $PH_3.BCl_3$ has been characterized by infra-red studies and measurement of the dipole moment; X-ray diffraction patterns of both $PH_3.BCl_3$ and $PH_3.BBr_3$ have been obtained (108).

Studies of this $PH_3.BX_3$ system have been extended recently (110) to include the mixed boron trihalides, which have been characterized by proton N.M.R. spectroscopy. Contrary to previous reports about the preparation of $PH_3.BF_3$ (58,111), this complex was not detected by N.M.R.; nor were the BF_2Cl, $BFCl_2$, BF_2I and BFI_2 adducts detected. It is perhaps hardly surprising that mixed adducts of the fluoride/iodide system were not detected since no trace of the free mixed halides could be found in an earlier study

(112). When CD_3PH_2 -- a stronger Lewis base -- was used the preparation and identification of the BF_3, BF_2Cl, and $BFCl_2$ adducts was successful, but there was still no evidence of the mixed fluoroiodide complexes.

In contrast to the fairly well known boron halide complexes, adducts of borane were not prepared until 1940 (109) when phosphine borane was isolated. A kinetic study of its formation in the vapour phase has been carried out (113), while more recently the complex has been characterized by X-ray crystallography (114), N.M.R., I.R. and Raman spectroscopy (115).

Considerable interest in the type of bonding between phosphorus and boron was generated when Parry and Bissot (116) reported the preparation of $PF_3.BH_3$. The existence of the compound was surprising since both PF_3 and BH_3 are weak in their Lewis behavior (117). To explain the formation of this adduct Graham and Stone (118) proposed that the strength of the donor acceptor bond is enhanced by the formation of a $d\pi-p\pi$ bond between the empty $d\pi$ orbitals on phosphorus and an H_3 group orbital with π symmetry on the borane entity. The validity of this model has been questioned recently by Paine and Parry (119) who prepared and characterized the halodifluorophosphine adducts of borane. They found, by measurement of the gas phase equilibrium constant, that the order of decreasing stability

of the complexes was: $F_2HP \gg F_3P > F_2ClP > F_2BrP > F_2IP$.

Earlier it had been found that in the presence of a solvent the base strength of PF_3 is about equal to that of PH_3, whilst in the absence of a solvent PF_3 is favoured as a stronger base (120).

This order is opposite to that expected if the inductive effect of X were to play a determining role in the stability of the complex. The data collected indicate that there is a decrease in the B-H force constant with decreasing bond stability. These facts are not consistent with the model proposed by Graham and Stone (118). From their model it is clear that electron density from the B-H bond is effective in the formation of a P-B bond, leading to a decrease in the force constant as the strength of the P-B bond increases. Thus Parry et al (119, 120) adopted a new model. It was proposed that the closer an acid could approach, the more the donor's lone pair would be distorted resulting in a stronger D-A bond. When the reference acid is borane, the reorganization energy is fairly small permitting a close approach to the donor. That PH_3 is a weaker donor than PF_2H was rationalized by assuming that in PH_3 the electron pair was largely S in character and was held more tightly to the phosphorus (121). With PF_2H, the presence of an internal hydrogen bond between the proton and the fluorines was postulated, thus allowing a "tighter

pyramid" to be formed. With a given expenditure of energy, BH_3 is thus permitted to approach more closely to PF_2H than to PF_3 and PH_3. This would more than compensate for the fact that the presence of fluorine atoms would tend to pull the lone pair towards phosphorus. Similarly has the order of the halodifluorophosphine complexes been explained (119).

A contribution to the relatively high stability of HF_2PBH_3 might come from the molecular structure which has been shown to be distorted (122). The borane group is tipped toward the hydrogen of the base, presumably because of electrostatic interaction. If X = halogen however, an increase in size would be expected to lower the stability of the complex.

Extensive studies have been carried out to characterize other substituted phosphine adducts. Techniques used include pyrolysis (122), N.M.R. (123-129), I.R. (130), Raman (131), calorimetry (132) and measurement of the dipole moments (133).

iv) Nitrogen Donors

Boron nitrogen compounds have been known for over a century, but attempts to study this branch of chemistry have been carried out only in the last thirty years. Wiberg (134) was one of the first to point out the similarities between the isoelectronic C-C and B-N systems. Many

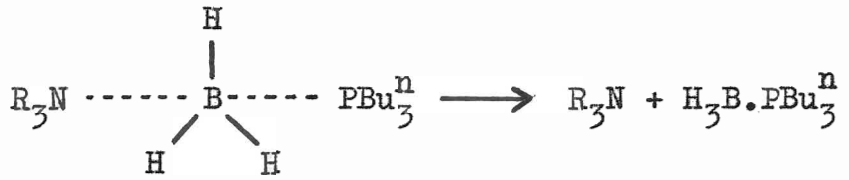
new compounds have been prepared, particularly of the boron halides and much of this work has been concerned with determining the nature of the D-A bond and the relative acceptor strengths of these Lewis acids.

N.M.R. has been used for just this purpose in studying acetonitrile adducts (29). The proton chemical shifts of CH_3CNBX_3 adducts, relative to tetramethylsilane decrease in the order $BBr_3 > BCl_3 > BF_3$ and show a direct relationship to the heats of formation of these complexes which were determined earlier (62, 135). Good correlation was also obtained with the dipole moments and I.R. carbonyl shifts of related adducts. It was proposed that all these measurements depended on the strength of the coordinate bond, thus suggesting the order of acceptor power to be $BBr_3 > BCl_3 > BF_3$. This order is in agreement with that proposed earlier by Brown and Holmes (57). It was appreciated however that the limitations of these methods prevented absolute conclusions from being drawn. The validity of the postulate was placed on a firmer basis when a structural determination revealed that BCl_3 formed a shorter -- and presumably stronger -- bond with CH_3CN than BF_3 (136). Calculation of the stretching force constants from vibrational analysis (137, 138) yielded similar results indicating that differences in reorganization energy could not solely account for the observed acceptor strengths of the boron trihalides.

The kinetics of coordinate bond formation have proved to be of considerable interest since no bonds are broken and the only rearrangements involve bending and stretching of bonds. Probably the earliest report of kinetic data on reactions involving dative bond formation is that of Lewis and Seaborg (139) who found the activation energy to be very small. This conclusion was later verified by Kistiakowsky and his co-workers (140-143) who also showed that the reaction of ammonia with BF_3 was much slower than the corresponding reactions using alkyl amines suggesting that the activation energy decreased with increasing alkyl substitution. Thus the relative reaction rates could be explained in terms of the basic strengths of the amines.

In a recent study (144) of the exchange of $CH_3CN.BX_3$ (X = F, Cl, Br) with excess CH_3CN it was concluded that the rate determining step is dissociation of the adduct. It seems unlikely that the mechanism is dictated by steric terms, as has been argued for some systems (145) since acetonitrile has a linear structure. An S_N2 mechanism may be destabilized by steric crowding around the boron atom in its five coordinate transition state. However such a mechanism has been postulated for the nucleophilic attack of an arylamine on $CH_3CN.BCl_3$, although the analogous BBr_3 system reacted via dissociation (146). A similar

mechanistic crossover was observed for the reactions of alkylamine boranes with Bu^n_3P in o-dichlorobenzene. The reaction of Me_3NBH_3 and Et_3NBH_3 proceeds through an S_N2 process which causes inversion at the reaction site (147).



The same mechanism prevailed when adducts of mono-substituted alkyl and aryl boranes -- having low steric requirements -- were used; but a first order S_N1 dissociation dominated the reaction of $Me_3NBH_2{}^tBu$ with Bu^n_3P (148).

Many other boron nitrogen systems have been studied. These include hydrazines (149, 150) nitrogen heterocycles (151) and complexes of tetrasulphur tetranitrides(152, 153). The reaction of the boron halides with ammonia and its derivatives is probably one of the most extensively studied fieldsin boron chemistry. As such it goes far beyond the scope of this thesis. Thus the interested reader is directed to the excellent reviews of Massey (49), Nöth (153) and Stone (23).

C. TRIMETHYLAMINE ADDUCTS

i) Trimethylamine Borane (TMAB)

The preparation and characterization of TMAB by the action of trimethylamine on borane carbonyl (BH_3CO)

was first reported by Burg and Schlesinger (154) who later extended their work (155) to similar complexes of methyl substituted boranes. They found, by following the rate of hydrogen chloride attack on the boron hydrogen bonds, that the stability -- towards dissociation of the B-N bond -- decreased as methyl substitution increased and that only in trimethylamine trimethyl borane was the B-N bond broken:-

$$(CH_3)_3N.B(CH_3)_3 + HCl \longrightarrow (CH_3)_3B + (CH_3)_3NH^+Cl^-$$

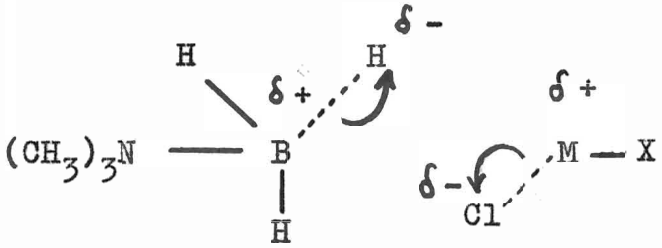
Several other studies (30, 118, 156-159) on TMAB and its derivatives have since been reported.

The comparison of the relative Lewis acid strengths of borane and boron trifluoride is interesting since the strength varies depending on the base used. Thus with dimethyl ether $BF_3 > BH_3$ (160, 161); when trimethylphosphine is the base, the order is reversed (162, 163) and when trimethylamine is the donor $BF_3 \eqsim BH_3$ (28, 63). The enthalpies of dissociation of the complexes are about equal (28) although some of the reported values (23) vary considerably. This may result from the uncertainty in the values of the heat of dissociation of diborane (164-166). It may be noted that diborane will not displace BF_3 from $(CH_3)_3NBF_3$ unless ether is present (167). A recent study of the absolute rate of formation of TMAB (168) indicates that

BH_3 is a weaker acid toward trimethylamine than BF_3, even though it is much less stabilized in its planar geometry than BF_3 (169, 170).

Halogen substitution of one or more boron protons in TMAB has been accomplished using hydrogen halides (155, 156), halogens (156) and boron trihalides (171) and dimethylchloramine (172). Increased chlorination caused the B-H stretching frequency to increase and shifted the boron and proton chemical shifts to lower field thus offering a means of detection. However reactivity towards chlorination decreases in the order TMAB > $TMABH_2Cl$ > $TMABHCl_2$ (173).

Two alternative mechanisms for the chlorination have been suggested. Nöth and Beyer (156) proposed a heterolytic process involving hydride transfer with a concerted halogen transfer in the opposite direction:-



This mechanism is particularly effective in explaining the action of chlorinating agents such as the chlorides of antimony and mercury which can behave as Lewis acids by functioning as hydride acceptors.

A free radical mechanism has been postulated by

Wiggins and Ryschkewitsch (173). The initial step would be cleavage of the bond to chlorine:-

$$ClM\text{-}Cl \longrightarrow ClM^{\bullet} + Cl^{\bullet}$$

followed by hydrogen abstraction at the B-H bond.

$$Cl^{\bullet} + DBH_2\text{-}H \longrightarrow DBH_2^{\bullet} + HCl$$

$$DBH_2^{\bullet} + Cl\text{-}M\text{-}Cl \longrightarrow DBH_2Cl + {}^{\bullet}MCl$$

In many cases, the activation energies for cleavage of the M-Cl bonds may be too high to account for the fairly rapid reaction observed; it therefore seems that this mechanism may be ruled out unless there is an energetically feasible route for initiation and maintenance of a long chain.

Fluorination of TMAB using anhydrous hydrogen fluoride is shown (174) to proceed vigorously in cold benzene to give, in stepwise fashion, $TMA.BH_2F$, $TMA.BHF_2$, $TMA.BF_3$ and $TMAH^{+}BF_4^{-}$. The proton chemical shifts of the mixed fluoroboranes occur to higher field of the parent compound suggesting that the acid strength decreases in the order $BH_3 \eqslantless BF_3 > BH_2F > BHF_2$. This surprising order is not readily explainable at present.

ii) Trimethylamine Boron Trihalides

Complexes of trimethylamine with boron trifluoride (175-177), boron trichloride (20, 178), boron tribromide

(179) and boron triiodide (180) are well known. Table 3 shows the B-N bond distances of the compounds which have been determined by X-ray crystallography (181-183) and microwave spectroscopy (184). Significant variations in the B-N bond lengths are observed with the result that no clear correlation can be drawn as to the B-N bond strengths within the series.

TABLE 3 The B-N Bond Distance in Trimethylamine Complexes

Lewis Acid	Crystal Structure Type	B-N Bond Length ^{o}A	Ref.
BH_3	-	1.65 ± 0.02	184
BF_3	Rhombohedral	1.585 ± 0.03	181
BF_3	"	1.636 ± 0.0004	184
BCl_3	Monoclinic	1.575 ± 0.011	183
BCl_3	"	1.610 ± 0.006	182
BBr_3	"	1.603 ± 0.02	182
BI_3	"	1.584 ± 0.025	182

Displacement reactions (118, 157, 185) show that free boron trihalides containing a heavier halogen displace a lighter halogen from its adduct while the reverse reaction occurs to a negligible extent. A bimolecular reaction mechanism was proposed (185) for the reaction of $(CH_3)_3NBF_3$ with BCl_3 at temperatures less than 200^{o}C, while above that

dissociation played a more important role:

$$(CH_3)_3NBF \longrightarrow (CH_3)_3N + BF_3$$

$$(CH_3)_3N + BCl_3 \longrightarrow (CH_3)_3NBCl_3$$

The importance of the latter mechanism was firmly established by Coyle (186) who used isotopically labelled $(CH_3.CH_2)_3N^{10}BF_3$ in an analogous reaction that showed B-N bond breakage above 60°C.

Infra-red (27, 187) and Raman spectra (27) were recorded and vibrational assignments of the observed frequencies were proposed. A recent vibrational study (182) suggests that the order of Lewis acidity toward trimethylamine is $BI_3 > BF_3 > BBr_3 > BCl_3$. This order was based on the B-N bond stretching force constants which are believed to involve only properties of the complexes themselves and not the energetics of their formation. The trend was rationalized (182) by the suggestion that the halogen atoms effectively repulsed the lone pair of electrons in the dative bond; it was argued that the repulsion would decrease as the B-X bond distance and the polarizability of X increased. High electronegativity was cited as the cause for the anomalous position of the fluoride.

N.M.R. has been extensively used (28, 30, 65, 187-189), to estimate the order of acceptor ability of the boron trihalides toward trimethylamine, and the results

support the order inferred from dipole moment determinations (69), displacements reactions (157) and mass spectral data (31), that order being $BI_3 > BBr_3 > BCl_3 > BF_3$. Recently, attention has been focused on the broad-line proton and fluorine N.M.R. spectra of solid $(CH_3)_3NBF_3$ (190) in an effort to examine molecular motion. This motion causes changes in the signal shape and relaxation time, and activation energies for the reorganization processes may be calculated from the variation in the proton linewidths. Calculated and observed second moments are shown in Table 4; there is obviously good agreement, even though the theoretical values were obtained by a method which allowed only an approximation of the second moments by considering the relative contributions of other atoms (191).

TABLE 4 Observed and Calculated Second Moments $(Gauss)^2$ for $(CH_3)_3NBF_3$ (190)

BF_3	$N(CH_3)_3$	Calc.	Obs.
R	S S	28	30 (68^oK)
R	R S	7.0 - 8.0	7.6 (109^oK)
R	R R	1.6 - 2.5	2.0 ($>160^oK$)

R: rotating; S: stationary; R S: methyls rotating, $N(CH_3)_3$ stationary; R R: methyls rotating, $N(CH_3)_3$ rotating.

The second moment transitions have been rationalized in terms of a model in which, at ambient temperatures, both the CH_3 and BF_3 groups rotate about their three-fold axes and the $N(CH_3)_3$ group rotates about the B-N bond. As the temperature is decreased, first the $N(CH_3)_3$ group stops, then the methyl groups stop, and finally the BF_3 group stops.

A measure of the electron contributing power of amines has been estimated by investigating the hydrolysis of adducts of BF_3 and BCl_3 (192, 193). The rate determining step may involve either breaking the B-N bond, or the boron-substituent bond depending on the system (194, 195). Heaton and Riley (196) proposed that pre-ionization of the boron-chlorine bond is an important process in the hydrolysis of $(CH_3)_3NBCl_3$ since the reaction is more rapid in solvents of high dielectric constant.

$$(CH_3)_3NBCl_3 \xrightarrow{\text{slow}} \left[(CH_3)_3NBCl_2\right]^+ + Cl^-$$

$$2Cl^- + 2\left[(CH_3)_3NBCl_2\right]^+ + 6H_2O \xrightarrow{\text{fast}} 2\left[(CH_3)_3NH\right]^+ Cl^- + 4HCl + 2H_3BO_3.$$

Similarly, the monohaloborane adducts of trimethylamine are believed (197) to undergo a boron-halogen bond ionization with the rates of solvolysis increasing in the order DBH $Cl_2 <$ $DBH_2Br <$ DBH_2I. This mechanism

is substantially different to that proposed (198) for the hydrolysis of TMAB in dilute hydrochloric acid, which involves the bimolecular attack of a solvated proton on the adduct molecule.

D. REDISTRIBUTION REACTIONS

i) Introduction

Redistribution reactions, named by Calingaert and Beatty (199) are many and varied; there are the slow distributions of alkyl ligands in tetralkyl lead mixtures:-

$$Pb^{*}Et_4 + Et_3PbCl \rightleftharpoons Et_3Pb^{*}Cl + Et_4Pb$$

which may have half lives of the order of hours or days, and the rapid scrambling of halogen atoms when boron trihalides are mixed.

$$\text{eg. } BCl_3 + BBr_3 \rightleftharpoons BBrCl_2 + BBr_2Cl$$

The best definition of a redistribution reaction is that of Skinner (200). "A redistribution reaction is one in which the bonds change in relative position, but not in type."

The free energy of thermoneutral reactions, in which there are only small changes in bond energies, depends on the entropy terms; thus a random distribution of ligands is expected.

The equilibrium composition of a random mixture can be calculated statistically: for a central atom M (functionality or valence = n) with M different types of ligands to be shared, the number of different compounds formed is:-

$$\frac{(n + M - 1)!}{n!\ (M - 1)!}$$

A number of experimental techniques are available for studying redistribution reactions. These include X-ray crystallography, I.R. and Raman spectrophotometry, N.M.R. and mass spectrometry and gas chromatography and are ably reviewed by Lockhart (201).

ii) Redistribution Reactions of the Boron Trihalides

The existence of the mixed trihalides of boron was not established with any certainty until 1954 when reactions of the mixed fluorochlorides (202) and chlorobromides (203) were studied.

The preparation of the boron bromoiodides by the action of hydrogen iodide on boron tribromide has been previously reported by Besson (204); replacement of bromine by chlorine in boron tribromide had been shown to occur with chlorine (205), arsenic and antimony trichlorides (206) and carbon tetrachloride (207). Although the only end product in each case was boron trichloride, it seems certain that the mixed halides were prepared, but

not detected. A special search by Forbes and Anderson (208) for the chlorobromides also failed to reveal their existence even though a wide variety of chlorinating agents were used.

Simple distillation and fractional condensation (203) at -50°C soon established that the mixed boron trihalides could not be separated because of disproportionation to form the simple trihalides; that they existed only in an equilibrium with their parent molecules in which the redistribution of halogen atoms was quite rapid at room temperature. The observed Raman intensities of an equimolar mixture of BCl_3 and BBr_3 show the near random distribution of halogen atoms expected in a thermoneutral reaction.

The rate constant of 5.0 $l.mole^{-1}$ $sec.^{-1}$ for the BF_3/BCl_3 system was evaluated (202) by following changes in the I.R. intensities using a fast scanning spectrometer (209), while the equilibrium constants for this and other systems were calculated from I.R. (210, 211), N.M.R. (212) and mass spectral data (213). Table 5 indicates reasonably good agreement between the values of K obtained by different methods.

Lindeman and Wilson (215) obtained gas phase vibration spectra for the exchange of the fluoride/chloride, fluoride/bromide and chloride/bromide systems. Assignments

TABLE 5 Equilibrium Constants for Halogen Redistribution Reactions

$$K = \frac{[BXY_2]\ [BX_2Y]}{[BX_3]\ [BY_3]}$$

X	Y	K	Method	Ref.
F	Cl	0.53	I.R.	210, 211
F	Cl	0.48	I.R.	210
F	Cl	0.58	I.R.	210
F	Cl	0.51	^{11}B NMR	212
F	Cl	1.6	Mass Spectrometry	213
Br	Cl	6.8	Raman	214
Br	Cl	7.8	I.R.	214
Br	Cl	5.5	^{11}B NMR	212

of the observed frequencies were in good agreement with those values calculated using force constants, bond lengths and bond angles measured for the pure halides (216, 217).

Recently, good agreement was found in the measurement (Table 6) of ionization potentials by Mass Spectrometry (218) and photoelectron spectroscopy (219), although the results have been interpreted differently.

Lappert and his co-workers (218) compared their experimental results with values calculated from molecular orbital theories and showed that π back-donation from

TABLE 6 The First Ionization Potentials of the Simple Boron Trihalides (eV)

Compound	Mass Spec. (218)	Photoelectron Spec. (219)
BF_3	15.57	15.95
BCl_3	11.67	11.73
BBr_3	10.62	10.65
BI_3	9.24	9.36

halogen to boron decreases in the series $BI_3 > BBr_3 > BCl_3 > BF_3$. They argued that the σ charge drift $B \rightleftharpoons X$ is the dominant factor in deciding overall bond polarity. However, the relative π stabilization, as measured from photoelectron spectroscopy (219), follows the order $BF_3 > BCl_3 > BBr_3 > BI_3$ and thus agrees with conclusions drawn from other experimental data (63, 220). Additional evidence for this order comes from (i) determination of the relative Lewis acidities (57, 69, 221), (ii) calculations on the reorganization energies (169), (iii) bond length measurements (222) and (iv) calculations on the vibrational force constants (223).

Nuclear Magnetic Resonance has proved to be very useful in studying the boron trihalide equilibria. Coyle and Stone (224) used fluorine-19 N.M.R. to measure the chemical shifts and coupling constants of fluorine

containing species. The chemical shifts which have been correlated (225, 226) with electron density at the fluorine atom, moved to lower field as fluorine was replaced, indicating that the inductive effect (dominated by electronegativity) is of less importance than the mesomeric effect. Thus there is π donation in the order $F > Cl > Br$.

A recent boron-11 N.M.R. study (112) of all binary and ternary mixtures -- except the fluoride/iodide system -- showed good agreement (Table 7) with the work of Coyle and Stone (224) and Gates et al (227). No attempt was made to relate the boron-11 chemical shifts to Lewis acidity (112) possibly because Armstrong and Perkins suggested (228) that the electron acceptor strength of a molecule cannot be related to either the electron density on the central atom or the B-X bond order.

Several other similar studies have been carried out on alkyl and aryl substituted boron halides (102, 229-231).

iii) <u>The Mechanism of Halogen Exchange</u>

The low activation energy for the redistribution reactions has led to the assumption that the mechanism for halogen exchange in free boron trihalides involves a four-centre boron-halogen bridged species (49):-

TABLE 7 Chemical Shift Data for the Boron Trihalides

Compound	$\delta^{19}F$(a)	$\delta^{11}B$(b)	$\delta^{11}B$(c)	$J^{11}B-^{19}F$(d)	$J^{11}B-^{19}F$(e)
BF_3	0		-10.0	15	14.5
BF_2Cl	-51.5		-19.8	34	33
$BFCl_2$	-99.0		-32.3	14	73
BCl_3		-46.5	-46.5		
BF_2Br	-68.4		-19.5	56	58
$BFBr_2$	-130.4		-29.0	108	121
BCl_2Br		-45.3	-44.7		
$BClBr_2$		-42.6	-42.3		
BBr_3		-39.1	-38.7		
BCl_2I		-36.2	-36.1		
$BClI_2$		-18.2	-18.1		
BBr_2I		-26.9	-26.3		
$BBrI_2$		-11.7	-11.0		
BI_3		+7.0	+7.9		
BFClBr	-114.8		-31.9	92	95
BFClI	-		-29.7		102
BFBrI	-		-26.4		189
BClBrI		-32.0	-31.6		

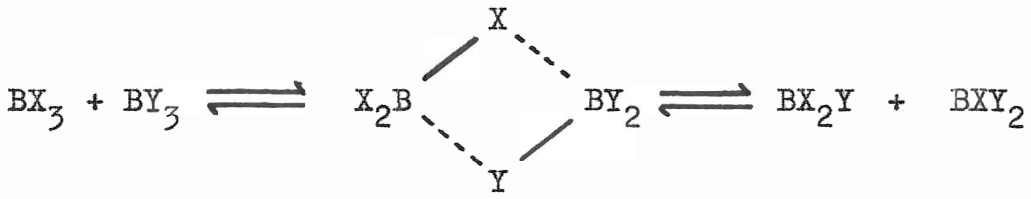
a) ppm increasing to high field of BF_3 as int. standard Ref. 224.

b) ppm relative to Et_2OBF_3 in methylcyclohexane converted from ppm relative to internal BCl_3 for comparison with (c). Ref. 227.

c) ppm relative to Et_2OBF_3 in methylcyclohexane. Ref. 112.

d) Hz. Ref. 224.

e) Hz. Ref. 112.



However, no dimers were detected (215) and it has been suggested that a slight degree of ionization may also be involved (203).

$$BX_3 + BY_3 \rightleftharpoons BBr_2^+ + BCl_3^-Br \rightleftharpoons BClBr_2 + BCl_2Br.$$

E. ADDUCTS OF THE MIXED BORON TRIHALIDES

The instability of the mixed boron trihalides towards disproportionation may well have discouraged investigations into the chemistry of their adducts. Until recently, few reports of any unsymmetrical boron Lewis acid complexes could be found in the literature. One of the earliest investigations of the effect of varying substituents on the boron atom was that of Burg and Green (176) who showed that substitution of fluorine by methyl groups reduced the relative Lewis acidity toward trimethylamine. Coyle and Stone (232) studied the effect of different alkyl groups on the acceptor power of boron trifluoride by Fluorine-19 N.M.R. in an effort to determine

the steric contribution to Lewis acidity. Mixed haloborane adducts of a variety of bases, including trimethylamine (155, 156), phosphine (233) and triethylamine (234) have been reported and the existence of mixed tetrahaloborate anions has been established (235, 236). More recently, the mixed boron trihalide adducts of dimethyl ether (237, 238), trimethylamine (239-243), picoline (244), esters (245), ureas (246) and phosphines (110,247) have been studied by N.M.R.

The separation of TMA.BF_2Br and TMA.$BFBr_2$ suggests that the mixed adducts are more stable to disproportionation than the free mixed acids. The mass spectra (31) of these adducts showed that as the proportion of bromine is increased, the B-N bond becomes stronger and that the mixed adducts preferentially lose bromine when a choice exists. This is good supporting evidence for the suggestion that π back-bonding between fluorine and boron is not destroyed on complex formation (70) and serves to weaken the B-N bond. Since complexation enhances the stability of the mixed trihalides, it may be possible to prepare trimethylamine adducts of BF_2I and BFI_2, although the latter have not been detected by N.M.R. in the free state (112, 248). Consistent with this observation is a recent report (110) that mixed fluoride/iodide adducts of phosphine could not be detected. Even with the use of CD_3PH_2 --

which, unlike phosphine allowed identification of the BF_3, BF_2Cl and $BFCl_2$ adducts -- the only complexes detected in the system were $CD_3PH_2.BF_3$ and $CD_3PH_2.BI_3$.

F. RESEARCH PROPOSAL

Trimethylamine complexes of boron trihalides are ideal adducts to work with since they are fairly stable and can be handled in air without any special precautions. After the characterization of some of the mixed adducts (239) and the isolation of two of them (242) a logical attempt to prepare and characterize the unknown binary and ternary mixed adducts, along with their separation seems in order.

The mechanism of halogen exchange presents an intriguing challenge and it is felt that this might be elucidated through the use of labelled adducts containing boron-10. In this way, reactions may be carried out with the boron trihalides -- containing isotopically natural boron -- to see if the B-N bond breaks during halogen exchange. Similarly could gas phase reactions, either of two adducts, or one adduct and a boron trihalide be carried out. The need for the presence of an excess of a Lewis acid may be tested by using other electron acceptors such as $AlCl_3$ or $SiCl_4$, while any contribution from an ionic mechanism can be estimated by using ions such as BX_4^- and X^-(X = Halogen).

CHAPTER II

EXPERIMENTAL

A standard pyrex glass high vacuum line (249-251) was used for the manipulation of gases and volatile liquids. Stopcocks and joints were greased with Apiezon N grease and pressures were measured using a Bourdon gauge as a null indicator. A nitrogen filled dry box was used to provide an inert atmosphere for handling air and moisture sensitive solids.

A. REAGENTS

i) Trimethylamine

Trimethylamine (Matheson) was fractionated under vacuum from a trap at -78°C to a trap at -196°C, the initial and final cuts being rejected each time. It was stored as a gas in a bulb on the vacuum line.

ii) Boron Trihalides

Boron trifluoride (Matheson) and boron trichloride (Matheson) were vacuum distilled several times and stored at ambient temperatures, the former as a gas, the latter as a liquid.

Boron tribromide (Alfa Inorganics) was shaken with mercury to remove free bromine and vacuum distilled at -78°C.

Boron triiodide (Alfa Inorganics) was used without further purification.

Boron-10 trifluoride (isotopic purity = 96%) was prepared by the action of heat on the stable calcium fluoride-boron trifluoride adduct (Oak Ridge National Laboratories). Typically, 0.02 moles of $CaF_2{}^{10}BF_3$ were placed in a stainless steel tube which was evacuated. The temperature was slowly raised to 300°C using a heating tape and the boron trifluoride evolved was collected in a trap at -196°C. It was purified by vacuum distillation and used immediately.

The preparation of boron-10 triiodide was attempted as a two stage synthesis from $^{10}BF_3$ following the method of Brauer (252). The first step involved preparation of labelled lithium borohydride ($Li^{10}BH_4$) from the reaction of lithium hydride (Research Inorganic Chemicals Corp.) with boron trifluoride diethylether in an autoclave at 120°C.

$$4\ LiH + {}^{10}BF_3.OEt_2 \longrightarrow Li^{10}BH_4 + 3LiF + Et_2O$$

The second part of the synthesis involved preparation of boron-10 triiodide by the direct action of iodine

on $Li^{10}BH_4$. Unfortunately the yields were so low as to render this method unsatisfactory.

iii) Trimethylamine Boron Trihalide Adducts

Trimethylamine borane (TMAB) (Callery Chemical Company) was purified by vacuum sublimation at room temperature.

DBX_3 complexes (D = trimethylamine) were prepared by the direct combination of reactants on the vacuum line in a synthesis vessel similar to that described earlier by Miller (253). Equimolar quantities of trimethylamine and BX_3 (X = F, Cl) were condensed from a calibrated bulb into the vessel at liquid nitrogen temperature. The mixture was warmed to room temperature very slowly and allowed to stand. Boron tribromide was measured from a tared burette, whilst boron triiodide was weighed into the flask. Excess trimethylamine was used in both cases. For the preparation of DBI_3 a solvent, methylene chloride, was condensed onto both reactants to ensure more intimate contact. This was removed along with excess base by pumping after one hour at room temperature. With the exception of DBI_3, the adducts were purified by vacuum sublimation. Their melting points, after purification are listed in Table 8. Included in the table, for sake of comparison are the melting points of a binary mixed adduct and a ternary mixed adduct.

TABLE 8 Melting Points of some Trimethylamine Boron Halide Complexes °C

Adduct	Found	Literature Value	Ref.
DBF_3	138-139	138	157
$DBCl_3$	239-240	238-240	157
$DBBr_3$	238-240	239	157
DBH_3	92-93	94	254
DBHClBr	130-134	-	-
$DBClBr_2$	224-228	-	-

As the atomic weight of the halogen increased, so did the temperature necessary for vacuum sublimation. Indeed, the temperatures required were:- DBF_3 : 45°C; $DBCl_3$: 80°C; DBHClBr : 90°C; $DBClBr_2$: 110°C; $DBBr_3$: 170°C. Attempts to purify DBI_3 by vacuum sublimation failed because the complex decomposed at 300°C, contrary to a report by Clippard (182) who successfully sublimed the adduct at 70-80°C. Purification by recrystallization from pentane -- containing a little cyclohexene to remove free iodine -- was not considered practical since only tiny yields were obtained. The adduct was therefore used as prepared.

Boron-10 labelled complexes

$(CH_3)_3N^{10}BF_3$ was prepared by direct combination of the reactants and purified by sublimation. The other adducts were prepared by displacement of fluorine using a free boron trihalide.

$(CH_3)_3N^{10}BCl_3$ was prepared by bubbling boron trichloride (natural abundance boron) from a lecture bottle through a solution of about 0.01 moles $(CH_3)_3N^{10}BF_3$ in methylene chloride. The reaction was followed by N.M.R., a spectrum being recorded every five minutes. After 20 minutes, there was still some $(CH_3)_3N^{10}BFCl_2$ even though a large excess of BCl_3 was present. To ensure that complete displacement occurred, the reaction flask was left to stand for 24 hours at ambient temperatures. The solvent was removed under vacuum and the product sublimed at 80°C.

$(CH_3)_3N^{10}BBr_3$. A calculated excess of boron tribromide (natural abundance boron) was condensed onto a freshly prepared solution of $(CH_3)_3N^{10}BF_3$ in methylene chloride. When the N.M.R. spectrum revealed only the presence of the required product, the solvent was removed by evacuation and the complex was purified.

$(CH_3)_3N^{10}BI_3$. Because of the disappointing yields in the preparation of $^{10}BI_3$, the trimethylamine adduct was

also prepared by displacement of fluorine from $(CH_3)_3N^{10}BF_3$ using BI_3 (natural abundance boron). Separate ice cold solutions of $(CH_3)_3N^{10}BF_3$ and BI_3 were prepared. Portions of BI_3 solution were added to the adduct solution using a hypodermic syringe. A vigorous reaction occurred, BF_3 being evolved. Additions were continued until the N.M.R. spectrum showed that only $(CH_3)_3N^{10}BI_3$ was present. Some decomposition had occurred as evidenced by the violet colour of iodine in solution. Purification was a problem. Sublimation was not possible; recrystallization was not practical. Volatile impurities (iodine and excess boron triiodide) were removed by pumping on the mixture for several hours at 50°C. The brown powder showed no impurities in the proton N.M.R. spectrum and was stored in an evacuated desiccator.

Mixed adducts

a) Binary mixed adducts

Binary mixed adducts were prepared in a manner similar to that described by Hartman and Miller (239). Suitable portions of a boron halide solution were added to an N.M.R. tube containing an adduct solution. Best results were obtained when the free Lewis acid contained a heavier halogen than that bound in the adduct. The resulting mixtures were studied by proton N.M.R. spectroscopy

at ambient temperatures. The products were identified by varying the relative concentrations, and by use of the boron-11 decoupler.

Following the successful separation (242) of the mixed fluorobromide adducts, an attempt was made to prepare complexes of the fluoride/chloride system. A mixture enriched in $(CH_3)_3NBF_2Cl$ and $(CH_3)_3NBFCl_2$ was prepared by the addition of boron trichloride to $(CH_3)_3NBF_3$ solution, the reaction being followed by N.M.R. The solvent was removed by evaporation under vacuum and unsuccessful attempts were made to separate the mixed adducts from the starting material by fractional sublimation and recrystallization. Sublimation was more useful than recrystallization, but since the parent adducts sublimed at similar temperatures, the difference being about 30°C, it is not surprising that the mixed adducts could not be separated in this manner. One system which might allow successful separation of mixed adducts by vacuum sublimation would be the chloride/iodide system since $(CH_3)_3NBI_3$ does not sublime. It would therefore seem reasonable to expect different rates of sublimation of the two mixed adducts.

Halogens (156, 240), hydrogen halides (155, 156), boron trihalides (156, 171) and other reagents (173) have successfully been used to replace the borane hydrogen in amine borane complexes. In most cases, either one or all

hydrogen atoms were displaced. It was thought that this presented a suitable alternative method for the preparation of mixed adducts, providing halogenating agents were selected carefully.

The reaction of TMAB with bromine and iodine

Separate methylene chloride solutions of bromine, iodine and TMAB were prepared. Portions of a halogen solution were added to separate adduct solutions in round bottomed flasks. The bromine was rapidly decolourised; the iodine reacted more slowly. The progress of the reaction was followed by N.M.R. and showed that bromine would displace all borane protons in a stepwise manner to form $(CH_3)_3NBBr_3$, while the reaction with iodine resulted only in $(CH_3)_3NBH_2I$.

Separate solutions of $(CH_3)_3NBH_2Br$ and $(CH_3)_3NBHBr_2$ were prepared by carefully monitoring the amount of bromine added. To each was added excess iodine and the mixtures were heated under reflux for several days. The system $(CH_3)_3NBH_2Br/I_2$ showed the presence of a small new peak in the N.M.R. spectrum. This was assigned to $(CH_3)_3NBHBrI$. No new products were detected in the other reaction.

When bromine and chlorine were separately added to $(CH_3)_3NBH_2I$, the iodine was immediately displaced, and the products were $(CH_3)_3NBBr_3$ and $(CH_3)_3NBCl_3$ respectively.

The reaction of $(CH_3)_3NBH_2Cl$ with bromine

$(CH_3)_3NBH_2Cl$ was prepared by bubbling hydrogen chloride through a methylene chloride solution of TMAB. Excess HCl and the solvent were pumped off under vacuum and the required product again dissolved in methylene chloride. Small portions of a bromine solution were added. Each addition of bromine caused partial collapse of the $(CH_3)_3NBH_2Cl$ resonance and the growth of a new peak assigned to $(CH_3)_3NBHClBr$. Further additions of bromine resulted in the formation of a 1 : 1 : 1 : 1 quartet which was assigned to $(CH_3)_3NBClBr_2$. Bromine additions were continued until the quartet was the only detectable resonance. The solvent and excess solvent were evaporated under vacuum and the crude product was purified by vacuum sublimation at 100°C. The I.R. and Mass Spectra were obtained, and the melting point range determined. The melting point (Table 8) was found to be in the range 224-228°C and is felt to be rather anomalous since both parent adducts have similar melting points in the range 238-240°C. This mixed adduct has been prepared previously (240), although experimental details were not published at that time.

b) Ternary mixed adducts

Ternary mixed adducts were prepared in solution by condensing equimolar quantities of three different boron trihalides into an N.M.R. tube followed by the

appropriate amount of trimethylamine and solvent. The tube was sealed and warmed to ambient temperatures before its contents were studied.

$(CH_3)_3NBHClBr$ was prepared by the action of bromine solution on $(CH_3)_3NBH_2Cl$. Additions of bromine were ceased when the N.M.R. spectrum indicated that only the required product was present. Purification was effected by vacuum sublimation at 80°C; I.R., and Mass Spectra were obtained and the melting point range obtained (Table 8).

iv) Tetraalkylammonium Salts

The tetraalkylammonium salts listed in Table 9 were used without further purification.

TABLE 9

Compound	Supplier
$Bu_4N^+Br^-$	Pfaltz & Bauer
$Bu_4N^+I^-$	Eastman Kodak
$Et_4N^+OAc^-$	Pfaltz & Bauer
$Et_4N^+BH_4^-$	Alfa Inorganics
$Et_4N^+Cl^-$	Eastman Kodak
$Et_4N^+F^-$	Pfaltz & Bauer
$Et_4N^+NO_3^-$	Pfaltz & Bauer

Tetraalkylammonium tetrahaloborates (halogen = F, Cl, Br) were prepared using the method of Schrobilgen (246). Tetrabutyl salts were preferred to tetraethyl salts since they were invariably more soluble in methylene chloride, although their N.M.R. resonances might occasionally have masked possible mixed adducts.

v) Solvents and N.M.R. References

Reagent grade methylene chloride (British Drug Houses) was fractionated before use and allowed to stand over Linde type 4A molecular sieves. Chloroform (British Drug Houses) was allowed to stand over molecular sieves. Ethanol free chloroform was prepared, when required, by washing the solvent with three times its own volume of water. It was dried using magnesium sulphate and phosphorus pentoxide (12 hours) and distilled.

Tetramethylsilane (Stohler Isotope Chemicals, and Merck, Sharpe and Dohme) and trichlorofluoromethane (K and K Laboratories) were purified by vacuum distillation and stored as gases on the vacuum line.

vi) Other Reagents

Hydrogen halides (halogen = Cl, Br and I) and arsenic trichloride were purified by vacuum distillation. Aluminium chloride, silicon tetrachloride, phosphorus trichloride and pentachloride were used without further

purification as were other general laboratory reagents.

B. SAMPLE PREPARATION

Reactions that would occur rapidly at room temperatures were generally carried out by adding small increments of one reactant to a solution of the other, recording an N.M.R. spectrum between each addition. In this way, the position and identity of overlapping resonances could be established.

When longer reaction times were required, the samples were prepared in 5 mm O.D. N.M.R. tubes on the vacuum line. Most samples were prepared in a qualitative manner by weighing approximately a suitable quantity of adduct into an N.M.R. tube which was then attached to the vacuum line. Known amounts of other reagents could be condensed into the N.M.R. tube from a calibrated bulb. Solvent and N.M.R. reference were added and the tube sealed while the contents were still at -196°C. If the second reagent was involatile, either a saturated solution of it was added to the adduct in the N.M.R. tube, or the solid was weighed in, the mixture being degassed and sealed under vacuum. Quantitative preparations were carried out in an identical manner except that all measurements were recorded accurately.

Dissociation reactions were carried out in a 25 cm long heavy wall glass tube. Mixtures of two adducts were weighed into the tube. The tube was evacuated, sealed and placed in an oven for 3 hours. The initial temperature of 300°C was found to cause much decomposition. This problem was overcome by reducing the reaction temperature to 160°C for boron trihalide adducts, and 120°C for borane adduct reactions. If the reaction required use of a boron trihalide it was either condensed into the tube at liquid nitrogen temperature, or in the case of boron triiodide weighed out under inert conditions. After the desired reaction time, the tube was cooled, cut open and solvent added. An N.M.R. spectrum of the contents was recorded.

C. INSTRUMENTATION

All spectra, unless otherwise stated, were obtained at ambient temperatures.

Fluorine-19 spectra were obtained on a Varian Associates DP-60 spectrometer operating at 56.4 MHz. The spectra were calibrated by the audio sideband method using the 2500 Hz sidebands from a Hewlett-Packard 200 C.D.R. audio oscillator which were 180° out of phase with the normal signals.

Proton spectra were obtained on a modified Varian

A-60 spectrometer operating at 60 MHz. An N.M.R. specialties H.D.-60 heteronuclear decoupler was used for boron-11 decoupling. All boron-11 nuclei were effectively decoupled by the pseudo "noise" method. A Hewlett-Packard H.P. 4204A decade oscillator was used to vary the input to a Wavetek 141 voltage controlled generator at 30 Hz. The generator supplied modulated audio sidebands for the 19.2 MHz ^{11}B frequency of the H.D.-60. Accurate measurement of the ^{1}H chemical shifts was achieved by calibration using the H.P. 4204A in conjunction with an Eldorado Electronics 224 frequency counter even though spectra were recorded on precalibrated paper. The spectrometer was equipped with a V-6040 variable temperature controller, high temperature calibration being achieved by the use of ethylene glycol. Spectral enhancement was provided, where necessary, using a Technical Measurement Corporation C1204 time averaging computer.

Infra-red spectra were recorded on a Perkin-Elmer Model 237B grating spectrophotometer. Solids were examined in either pellet form or as a nujol mull between potassium chloride plates.

Mass Spectra were obtained from an Associated Electrical Industries M.S.-30 Mass Spectrometer. Spectra were run at 70 eV and 20 eV using a direct insertion probe at the minimum temperature required for sample

volatilization and were calibrated against the known spectrum of perfluorokerosene run in beam 2.

CHAPTER III

RESULTS

A. THE REACTION OF TRIMETHYLAMINE ADDUCTS WITH BORON TRIHALIDES

a) Solution Reactions

i) Forward reactions

Previous work (239) has shown that mixed boron trihalide complexes result from the reaction of the BX_3 adduct with a free boron trihalide containing a heavier halogen. A series of similar reactions were carried out to confirm these findings, and to extend the series by covering all possible binary and ternary mixtures. Use of the boron-10 labelled adducts allowed the measurement of N.M.R. data that has not been previously reported. This data is summarized in Tables 10 and 11. The methyl proton signals of all adducts containing natural abundance boron are split by the boron-11 nucleus (spin = 3/2) into a 1 : 1 : 1 : 1 quartet.

Figure 1A shows the spectrum of the fluoride complex which consists of a partly resolved decet implying that the methyl proton signal is being split by the

TABLE 10 ^{1}H. N.M.R. Data for Trimethylamine Boron Halide Adducts

Me_3N complexed with:	δ p.p.m.[a]	δ Hz[a]	$J^{1}_{H-^{10}B}$ Hz	$J^{1}_{H-^{11}B}$ Hz
-- [b]	2.20	132.0	-	-
BF_3	2.60	156.0	*	*
BF_2Cl	2.71	162.5	*	1.8
BF_2Br	2.75	165.0	*	2.1
BF_2I	2.77	166.4	*	2.3
$BFCl_2$	2.83	170.0	*	2.1
$BFBr_2$	2.93	176.0	*	2.6
BCl_3	2.98	179.0	0.9	2.8
BFI_2	3.02	181.2	*	3.4
BCl_2Br	3.05	182.2	0.9	2.9
BCl_2I	3.08	184.7	0.91	3.0
$BClBr_2$	3.09	185.7	0.95	2.9
BBr_3	3.15	189.3	1.0	3.0
$BClI_2$	3.20	192.1	0.95	3.2
BBr_2I	3.21	192.5	1.0	3.2
$BBrI_2$	3.28	196.8	1.1	3.5
BI_3	3.35	201.0	1.16	3.5
BFClBr	2.89	173.4	-	#
BFClI	2.92	175.3	-	#
BFBrI	2.97	178.4	-	#
BClBrI	3.14	188.5	-	#

a: downfield from TMS
b: free Me_3N in CH_2Cl_2
*: not resolved
#: too dilute to observe

TABLE 11 ^{19}F. N.M.R. Data for Trimethylamine Adducts

Me_3N complexed with:	δ p.p.m.[a]	$J1_{H-}{}^{19}F$[b] Hz	$J10_{B-}{}^{19}F$ Hz	$J11_{B-}{}^{19}F$ Hz
BF_3	164.1	0.6	#	15.1
BF_2Cl	143.4	0.7	15.1	44.8
BF_2Br	134.0	0.8	19.6	54.2
$BFCl_2$	132.6	0.7	24.2	69.5
$BFBr_2$	120.8	0.8	30.4	89.3
BF_2I	119.6	0.9	21.8	65.8
BFI_2	*	0.8	*	*
BFClBr	126.0	0.7	-	78.0
BFClI	*	0.8	-	*
BFBrI	112.7	0.8	-	100.0

a: p.p.m. upfield from $CFCl_3$

b: ^{11}B decoupling required to observe

*: too dilute to observe

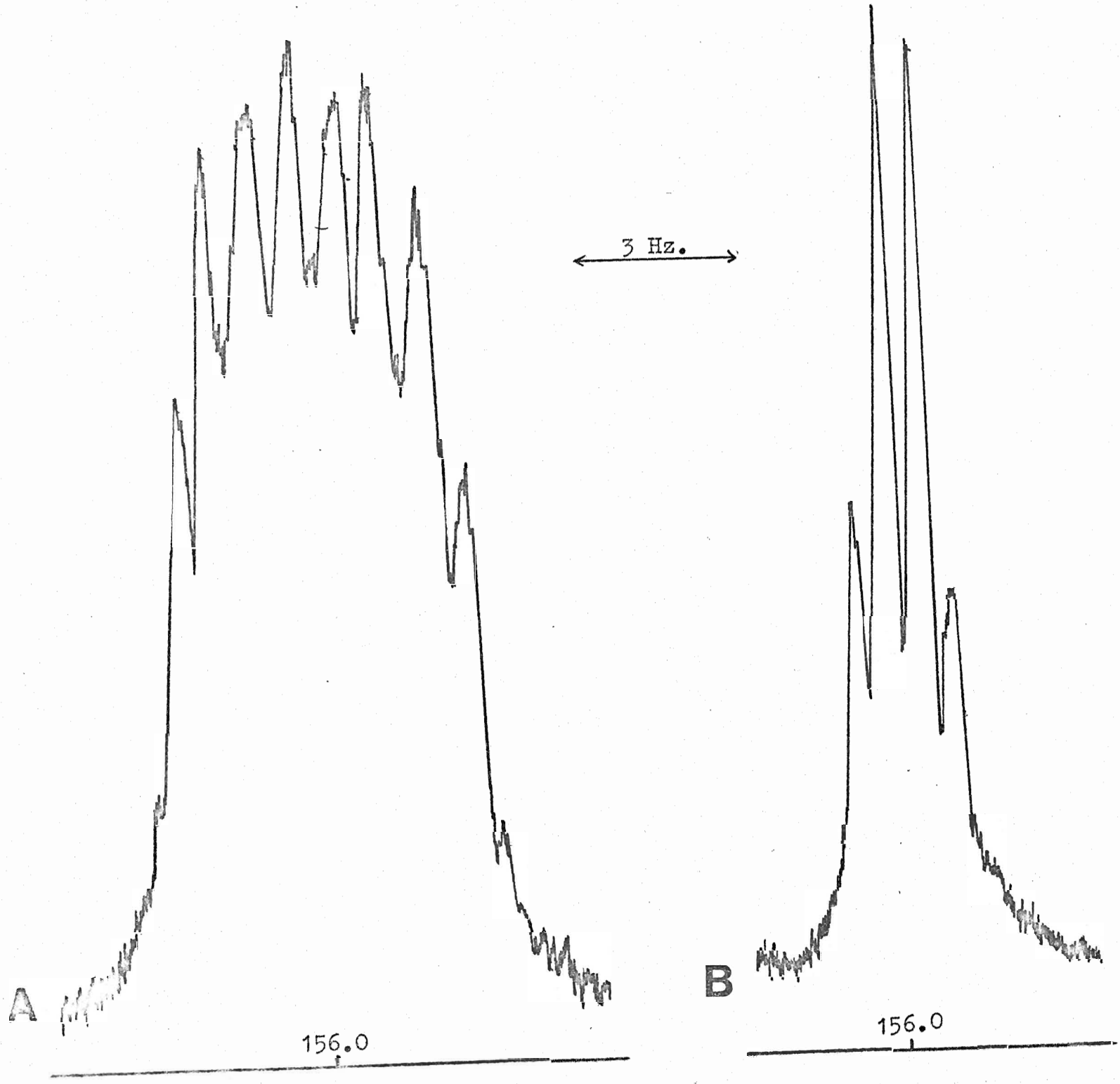
#: not resolved

FIGURE 1

^{1}H N.M.R. Spectrum of $(CH_3)_3NBF_3$

A) Normal

B) ^{11}B decoupled


3 Hz.
A
156.0
B
156.0

presence of other nuclei besides boron. Clague and Danti (187) obtained a broad signal containing eight peaks and concluded that hydrogen fluorine coupling was responsible for the extra splitting. Furthermore, they showed that by assuming $J^1_{H-^{19}F}$ = 0.8 Hz (equal to half $J^1_{H-^{11}B}$) then a decet of evenly spaced lines would result, the intensities correlating well with the observed spectrum. To clarify the point, the spectrum of $(CH_3)_3NBF_3$ was recorded (Figure 1B) while boron-11 was being decoupled. The results show a 1 : 3 : 3 : 1 quartet, $J^1_{H-^{19}F}$ = 0.6 Hz; the possibility of having hydrogen-nitrogen coupling thus seems very remote; this value agrees well with that of Heitsch (28) — who also found the coupling constant $J^{11}_{B-^{19}F}$ = 1.54 Hz, — and Massey and Park (266). Further evidence was collected by examining the BF_3/BX_3 (X = Cl, Br and I) adduct systems using boron-11 decoupling. In each case the signals corresponding to difluoro adducts were 1 : 2 : 1 triplets; those from monofluoro complexes were 1 : 1 doublets. Figure 2 shows examples of such systems.

The other trihalide adducts showed well resolved 1 : 1 : 1 : 1 quartets, with $J^1_{H-^{11}B}$ increasing in the order $BCl_3 < BBr_3 < BI_3$. Superimposed on each of these quartets was a weak septet attributable to the less abundant boron-10 (20% natural abundance) with spin I = 3. This septet was more clearly seen (Figure 2B (ii)) when

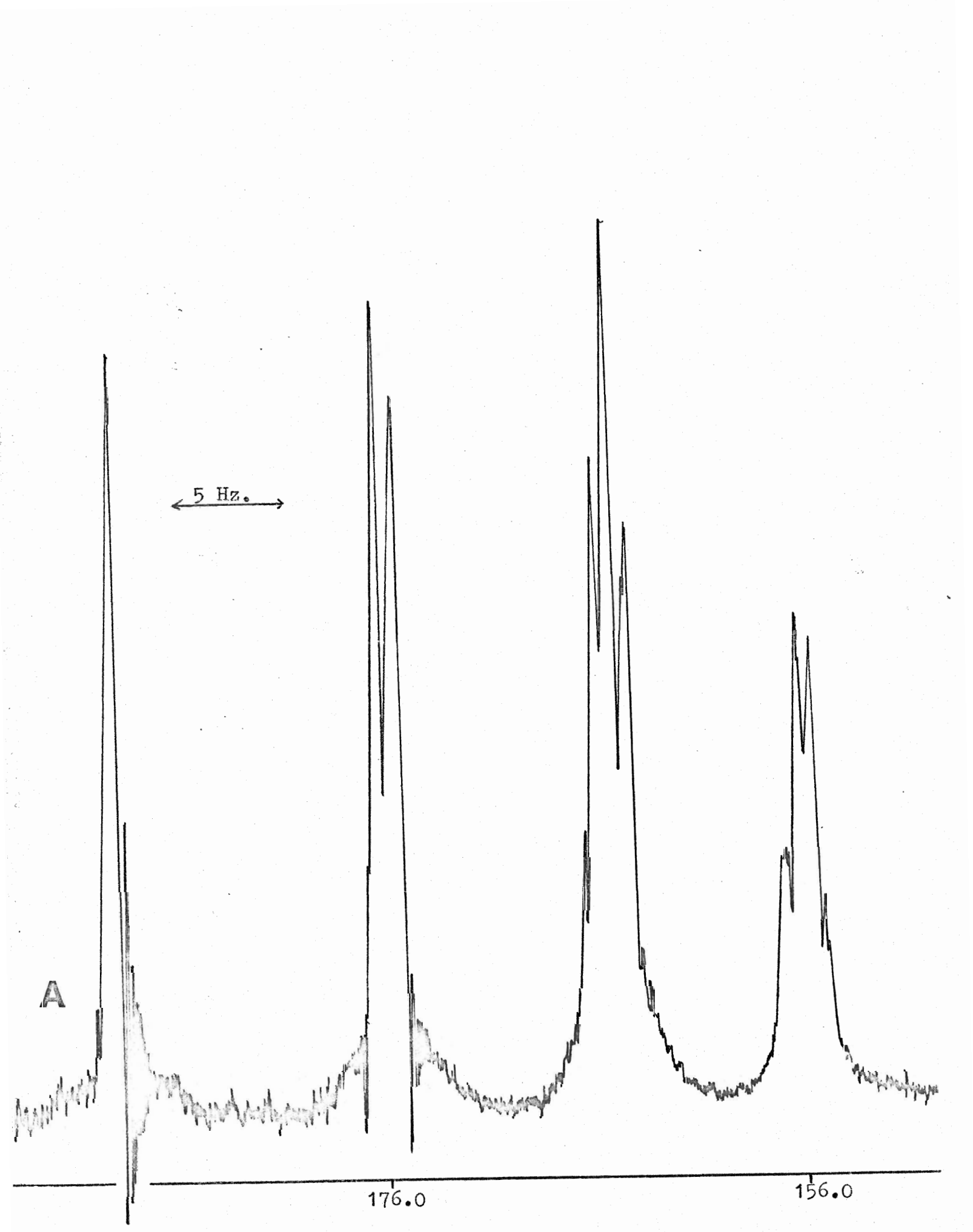
FIGURE 2

A) ^{1}H N.M.R. Spectrum of the $(CH_3)_3NBF_3/BBr_3$ system (^{11}B decoupled).

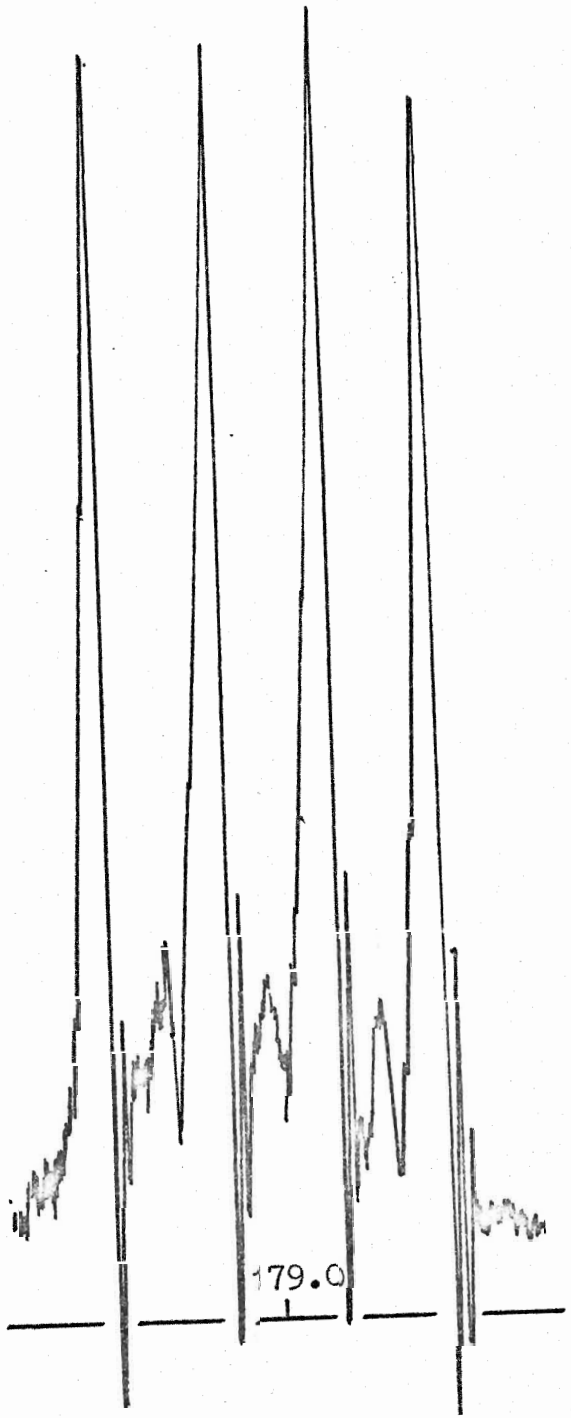
B) ^{1}H N.M.R. Spectrum of $(CH_3)_3NBCl_3$

i) Normal

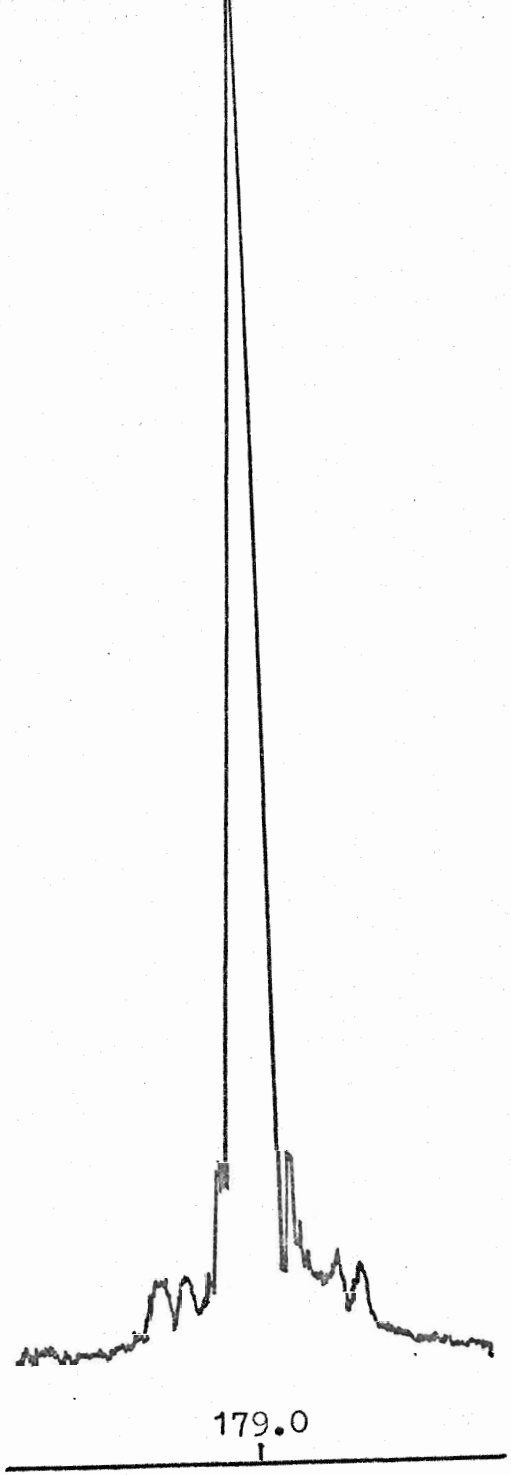
ii) ^{11}B decoupled


5 Hz.
A
176.0
156.0

B



5 Hz.



boron-11 was decoupled.

Most binary adduct systems show four overlapping quartets which can be identified and assigned by varying the concentration of the free boron trihalide. Typical spectra are shown in Figure 3.

The concentrations of the mixed fluoride/iodide adducts were very low compared with other systems, indicating that these complexes are possibly the least stable of the mixed trihalides. A study carried out by adding small increments of BI_3 solution to a solution of $(CH_3)_3NBF_3$ in CH_2Cl_2 showed that excess BI_3 reacted preferentially with the mixed adducts to give $(CH_3)_3NBI_3$, rather than with the $(CH_3)_3NBF_3$. It is apparent therefore that fluorine and iodine do not readily coexist on the same boron atom. The stabilizing influence of trimethylamine in allowing mixed halide formation can be appreciated since uncomplexed BF_2I and BFI_2 have not been detected by N.M.R. (212, 248) although their positive ions have been detected by mass spectrometry (218).

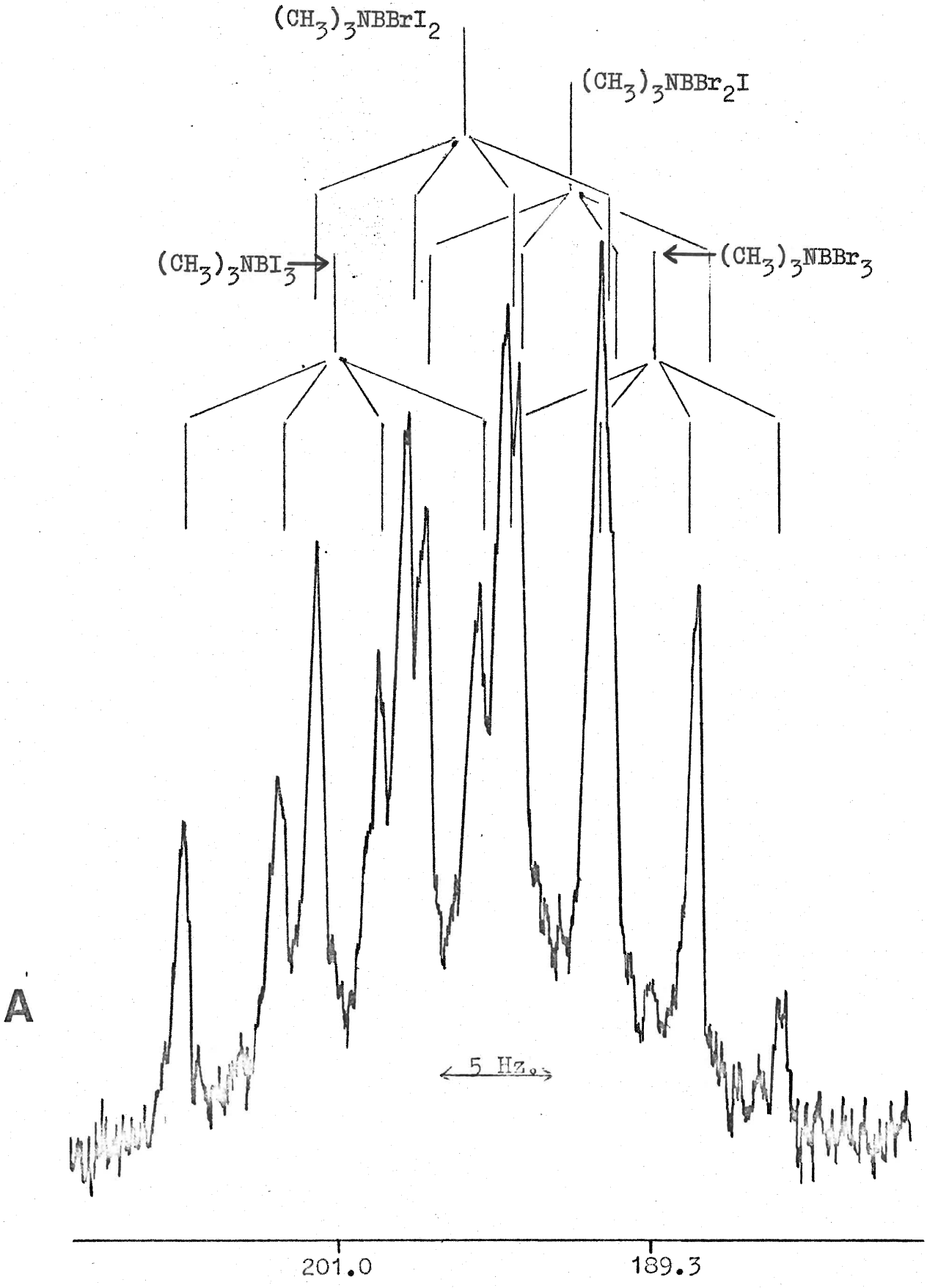
Spectral analysis of samples containing three different boron trihalides was difficult since the systems gave rise to a confusing array of overlapping multiplets. Use of the boron-11 decoupler simplified the spectra considerably and allowed identification of all possible binary adducts and the new ternary mixed adduct as well. The

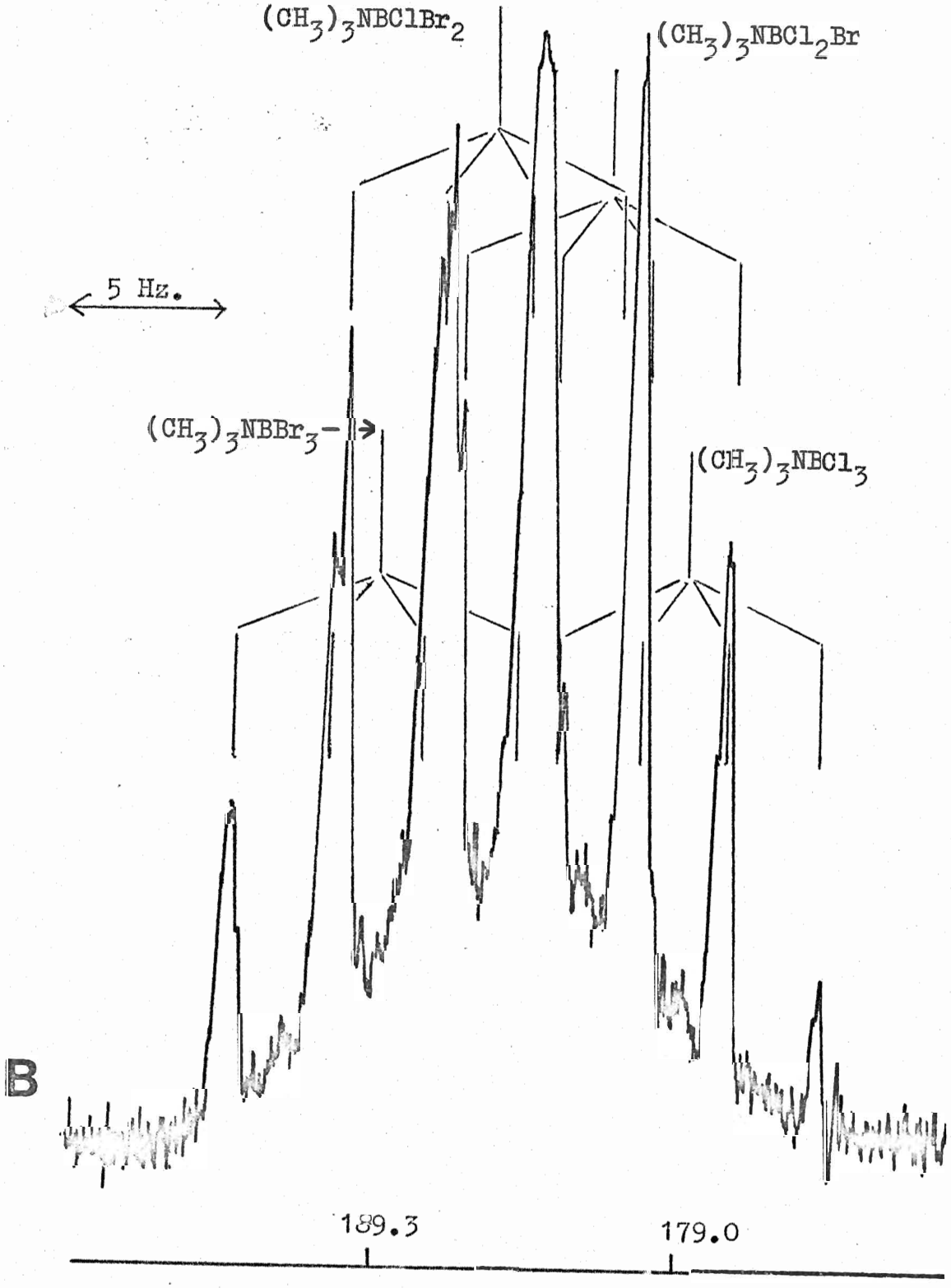
FIGURE 3

^1H N.M.R. Spectra of:-

A) The $(CH_3)_3NBBr_3/BI_3$ system

B) The $(CH_3)_3NBCl_3/BBr_3$ system


$(CH_3)_3NBBrI_2$
$(CH_3)_3NBBr_2I$
$(CH_3)_3NBI_3$
$(CH_3)_3NBBr_3$
A
5 Hz.
201.0
189.3


$(CH_3)_3NBClBr_2$
$(CH_3)_3NBCl_2Br$
5 Hz.
$(CH_3)_3NBBr_3^-$
$(CH_3)_3NBCl_3$
B
189.3
179.0

latter was characterised by its intermediate chemical shift and the fact that it absorbed as a doublet (under double irradiation) when fluorine was present. Figure 4 shows the system $(CH_3)_3NBF_3/BCl_3/BI_3$.

The fluorine-19 spectra were fairly simple, consisting of well separated quartets due to coupling with boron-11 (Figure 5). Most fluorine containing species were easily recognized, although the systems $(CH_3)_3NBF_3/BI_3$ and $(CH_3)_3NBF_3/BBr_3/BI_3$ had to be scanned several times with the computer in order to detect $(CH_3)_3NBF_2I$ and $(CH_3)_3NBFBrI$. However the latter technique in the time available to us was of little use in finding $(CH_3)_3NBFI_2$ and $(CH_3)_3NBFClI$; their low concentration obviously precluded their detection.

ii) Reactions using isotopically labelled boron

Boron-10 was used in the adducts in an attempt to determine whether B-N bond breakage occurred during halogen exchange. Boron-10 has a spin I = 3 (c.f. boron-11, I = 3/2) and can be easily recognized by its characteristic splitting pattern in the N.M.R.

A solution of $(CH_3)_3N^{10}BF_3$ in methylene chloride gave rise to a broad envelope with little resolvable fine structure. This was to be expected considering the splitting contributions from both boron-10 and fluorine-19, and

FIGURE 4

^{1}H N.M.R. Spectrum of:-

$(CH_3)_3NBF_3 + BCl_3 + BI_3$

i) Normal

ii) ^{11}B decoupled

a: $(CH_3)_3NBF_3$
b: $(CH_3)_3NBF_2Cl$
c: $(CH_3)_3NBF_2I$
d: $(CH_3)_3NBFCl_2$
e: $(CH_3)_3NBFClI$
f: $(CH_3)_3NBCl_3$
g: $(CH_3)_3NBCl_2I$
h: $(CH_3)_3NBClI_2$
i: $(CH_3)_3NBI_3$

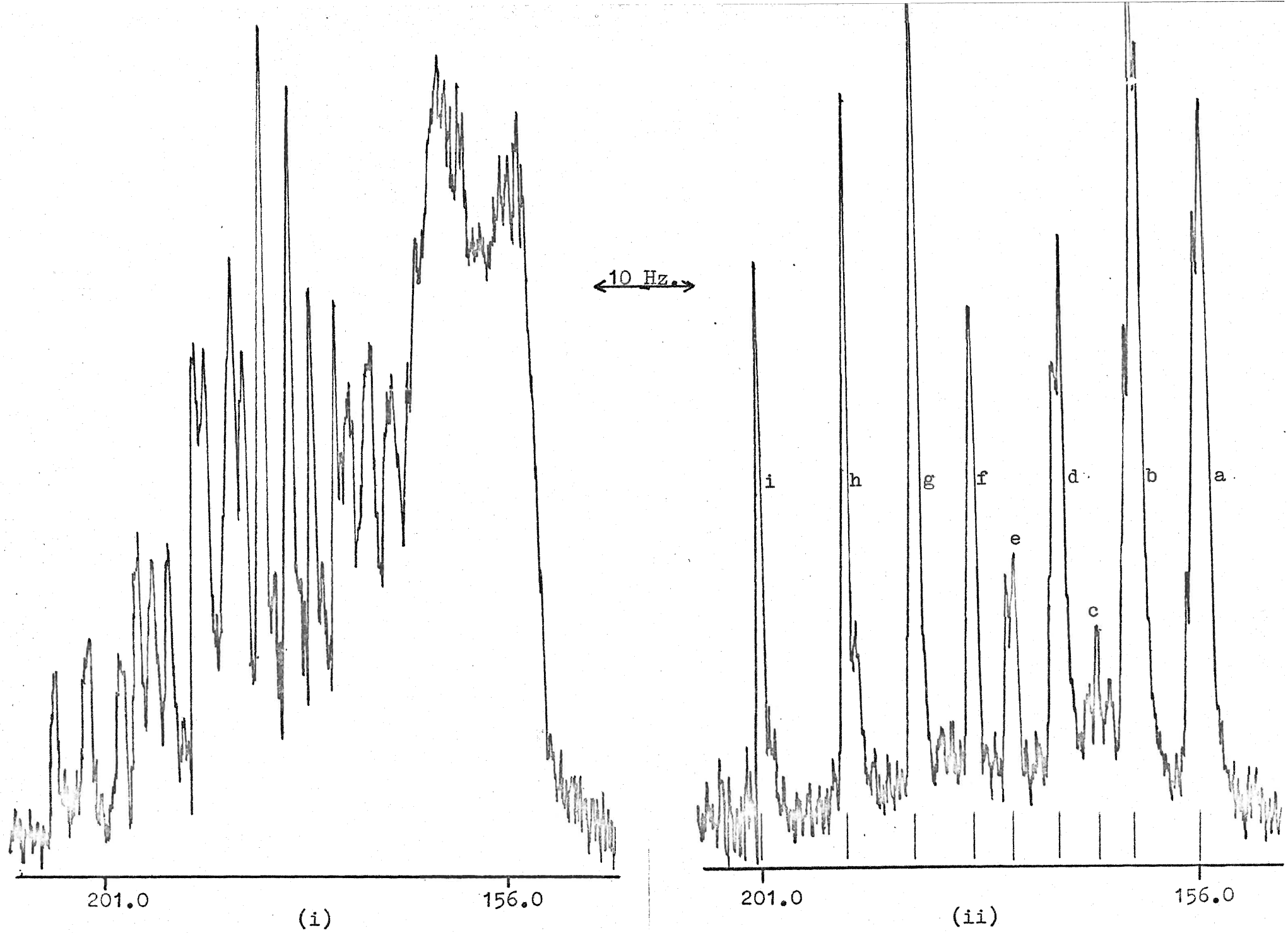
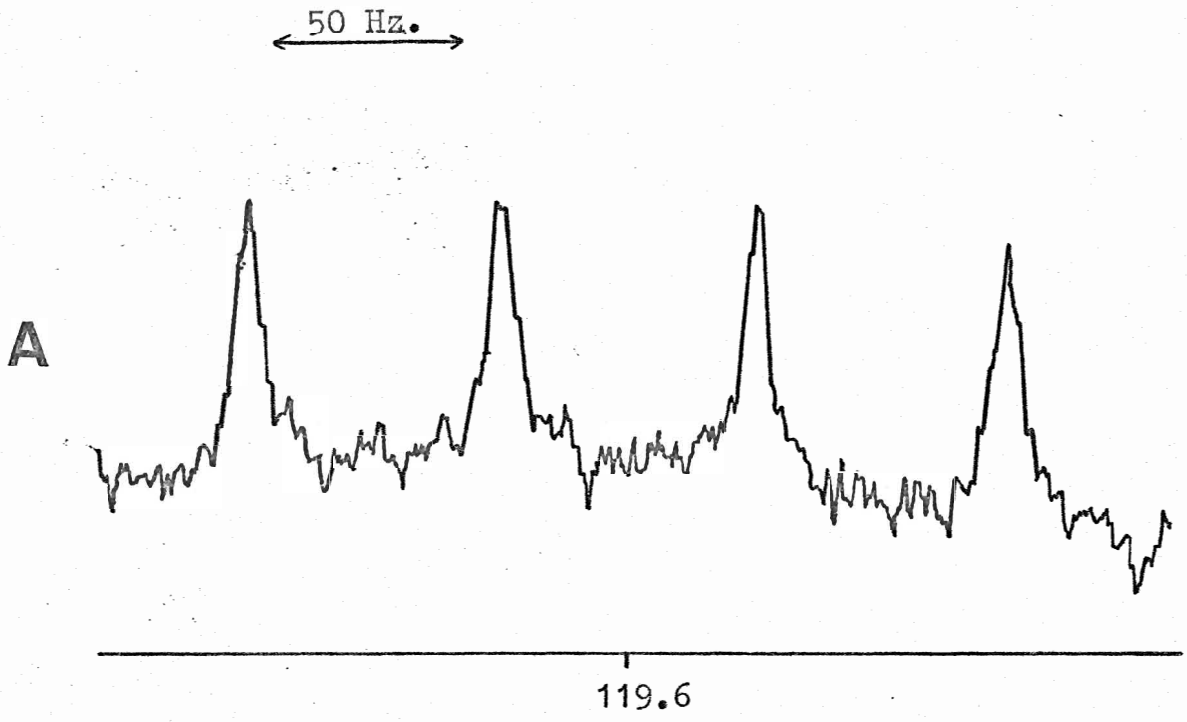

10 Hz
i
h
g
f
e
d
c
b
a
201.0
156.0
(i)
201.0
156.0
(ii)

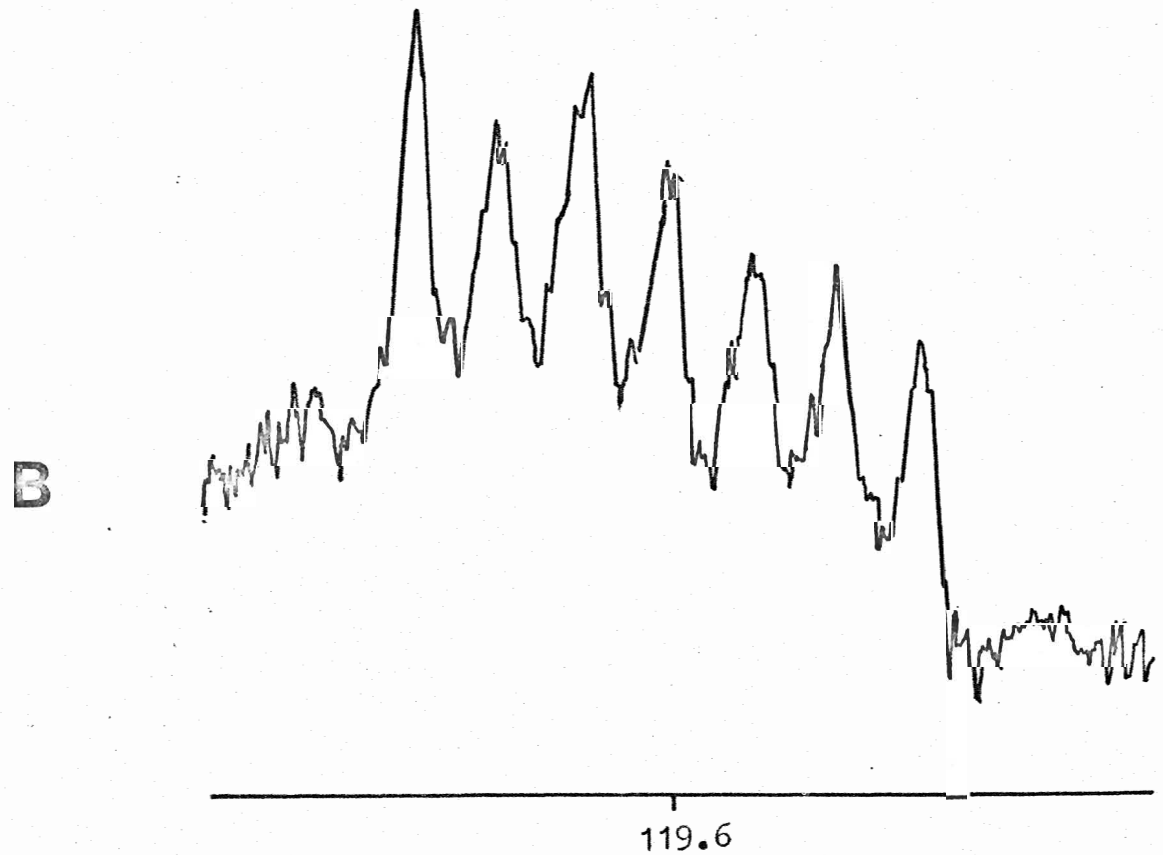
FIGURE 5

^{19}F N.M.R. Spectra of the adducts:-

A) $(CH_3)_3NBF_2I$ after 100 scans.

B) $(CH_3)_3N^{10}BF_2I$ after 79 scans.

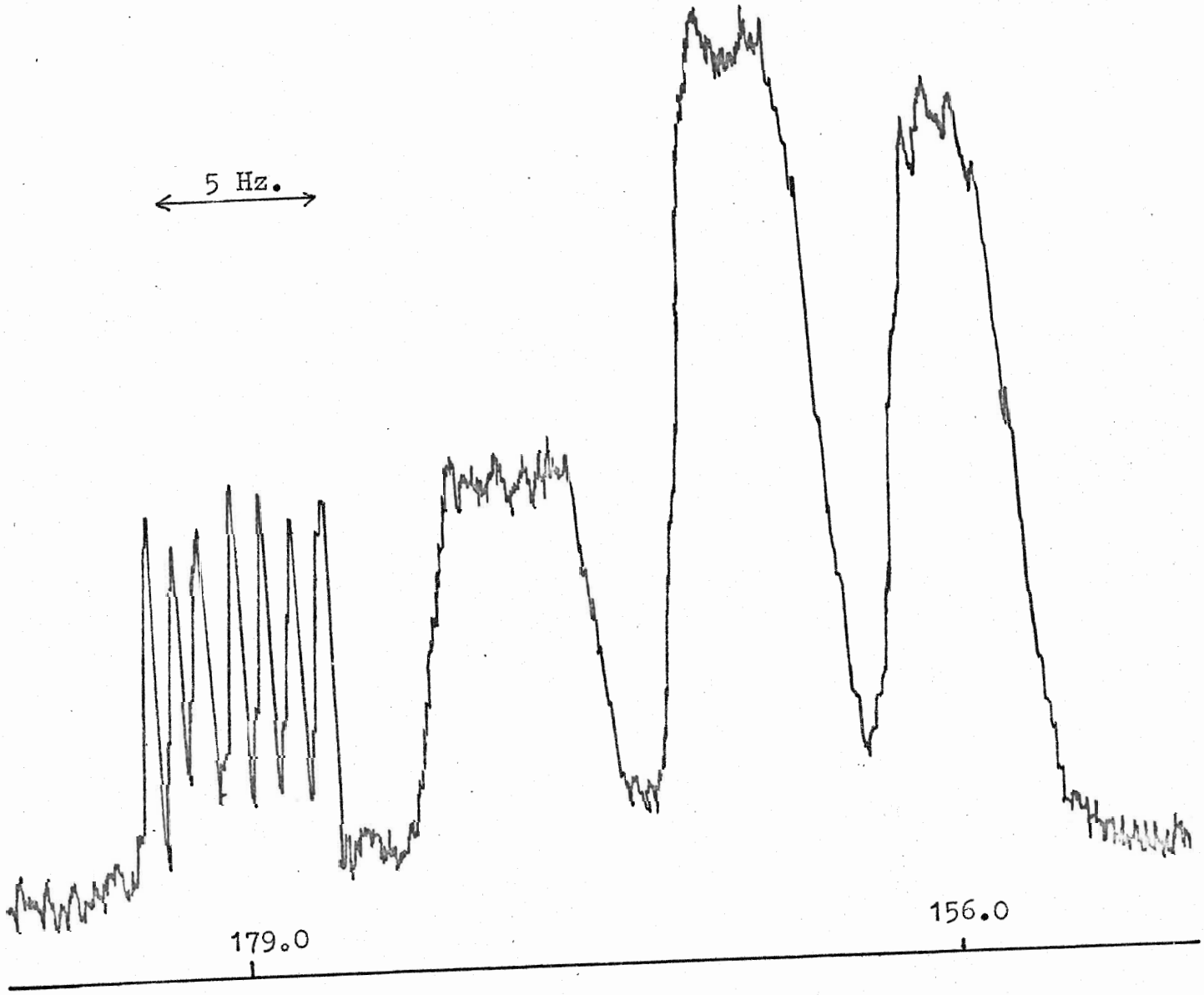

50 Hz.
A
119.6


B
119.6

the large quadrupole possessed by the boron nucleus (264). Use of the boron-11 decoupler resulted in the rise of a small sharp peak out of the top of the broad resonance. This is caused by the molecules containing boron-11 and is consistent with the 4% isotopic contamination of the starting material. All boron-10 adducts showed this tendency. The addition of boron trichloride solution (containing natural abundance boron) to the solution of $(CH_3)_3N^{10}BF_3$ resulted in the partial collapse of the BF_3 adduct resonance and the formation of two new peaks of chemical shifts corresponding to the difluorochloro, and monofluorodichloro adducts (see Figure 6). When the boron-11 decoupling frequency was used to irradiate the samples, the only change noticed was a small amount of sharpening. This strongly indicated that boron-11 was not being incorporated into the adduct during reaction. The observation was further supported when after several more additions of BCl_3 solution, a sharp characteristic seven-line multiplet formed at 179.0 Hz. This resonance was assigned to $(CH_3)_3N^{10}BCl_3$ (see Figure 6). This adduct was alone in having a well resolved septet. The other labelled boron halide complexes showed evidence of partial quadrupole collapse, in that neither were the spectral lines of the same intensity nor were they evenly spaced. Presumably $(CH_3)_3N^{10}BCl_3$ must have higher symmetry than the

FIGURE 6

^{1}H N.M.R. Spectrum of $(CH_3)_3N^{10}BF_3/BCl_3$


5 Hz.
179.0
156.0

other adducts.

Gillespie and co-workers have studied (264, 265) the temperature dependence of the spectra of boron trifluoride and have successfully matched observed and calculated line shapes for a series of temperatures. $(CH_3)_3N^{10}BBr_3$ and $(CH_3)_3N^{10}BI_3$ seem to show an intermediate line shape leading to the assumption that if the temperature were raised, more symmetry would result in the resonance. Figure 7 shows the change observed in the proton spectrum of $(CH_3)_3N^{10}BI_3$ as the temperature is raised to 70°C. The greater symmetry noted at the higher temperature confirms that quadrupole relaxation is a major factor in affecting the ambient temperature line shape.

Binary mixed adducts containing boron-10 were generally similar to the systems containing natural abundance boron, except for the expected difference in coupling constants. All could be prepared by adding BX_3 solution (natural abundance boron) to a solution of a labelled adduct since the B-N bond did not break during halogen exchange in solution. No attempt was made to prepare labelled ternary mixed adducts since it was felt that they would not be detected beneath the overlapping resonances of the binary adducts.

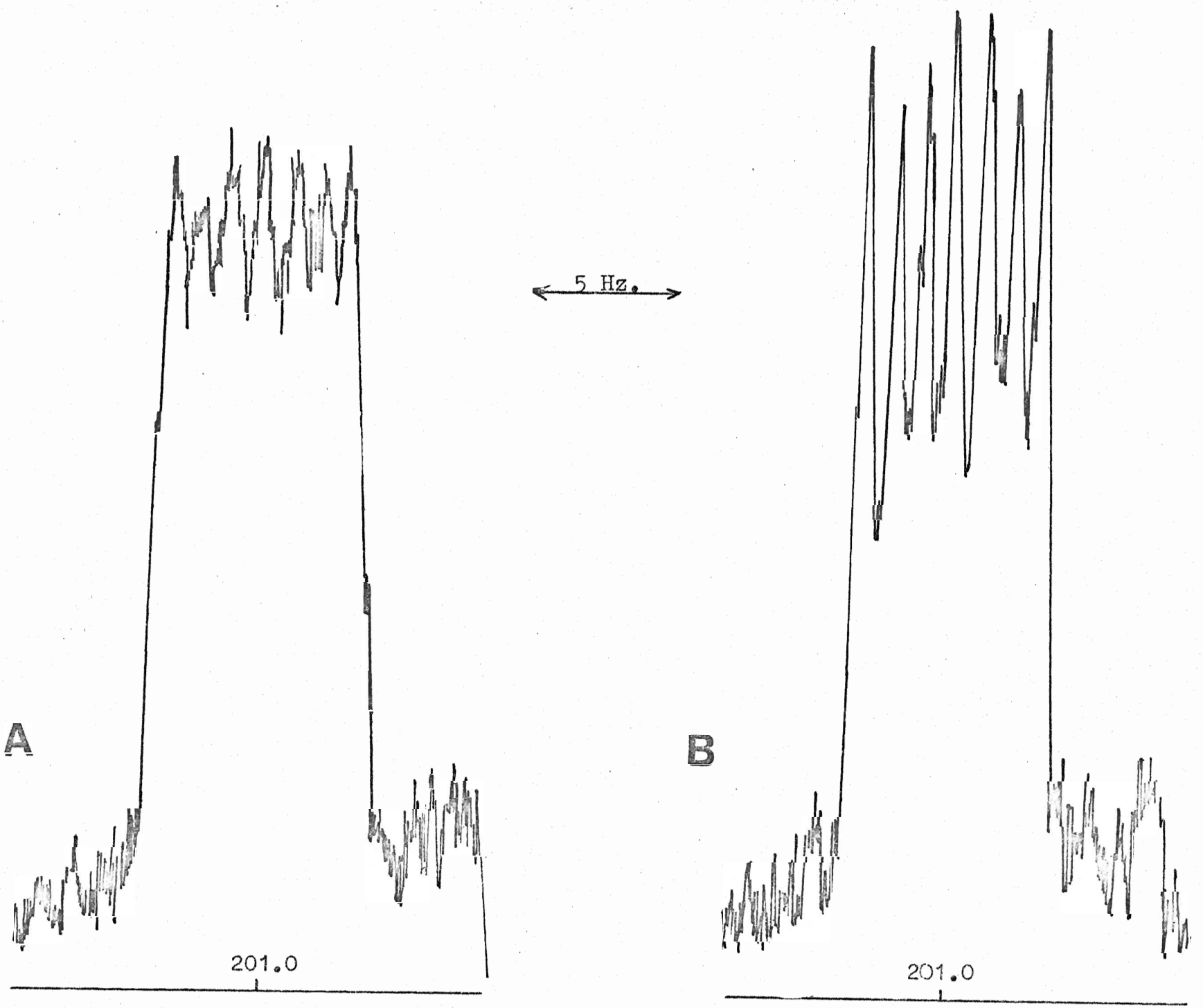
Fluorine-19 spectra showed the septets for most fluorine containing adducts. $J^{10}_{B-}{}^{19}_{F}$ was not resolved

FIGURE 7

^{1}H N.M.R. Spectrum of $(CH_3)_3N^{10}BI_3$

A) 37°C

B) 70°C


5 Hz.
A
201.0
B
201.0

for $(CH_3)_3N^{10}BF_3$, whilst the spectrum of $(CH_3)_3N^{10}BF_2I$ had to be scanned several times to detect an observable signal. The fluorine-19 chemical shifts were the same as for the adducts containing natural abundance boron.

iii) The isolation and identification of $(CH_3)_3NBClBr_2$

The preparation of $(CH_3)_3NBClBr_2$ has been adequately described above (Chapter II, Section IIIa) and need not be repeated here. The N.M.R. spectrum consisted of the required quartet with the correct chemical shift and coupling constant. The I.R. spectrum is shown in Figure 8 and the mass spectrum is listed in Table 12. Assignment of most ions was facilitated by the characteristic isotopic pattern displayed in the spectrum. Some clusters, for example m/e 174-167, did not give the required fit between theoretical and observed intensities. Calculations were made in an attempt to establish which ions were contributing to the isotopic pattern. The best results obtained indicated a mixture of 51.1% BBr_2^+ and 48.9% $C_2H_5NBClBr^+$. Similar calculations on other peaks thought to represent more than one ion gave the percentage contributions listed in the mass spectrum. Table 13 shows a comparison of abundance of ions formed from the decomposition of two similar mixed adducts, namely $(CH_3)_3NBFBr_2$ and $(CH_3)_3NBClBr_2$. Some trends of interest are apparent

FIGURE 8

The I.R. Spectrum of $(CH_3)_3NBClBr_2$

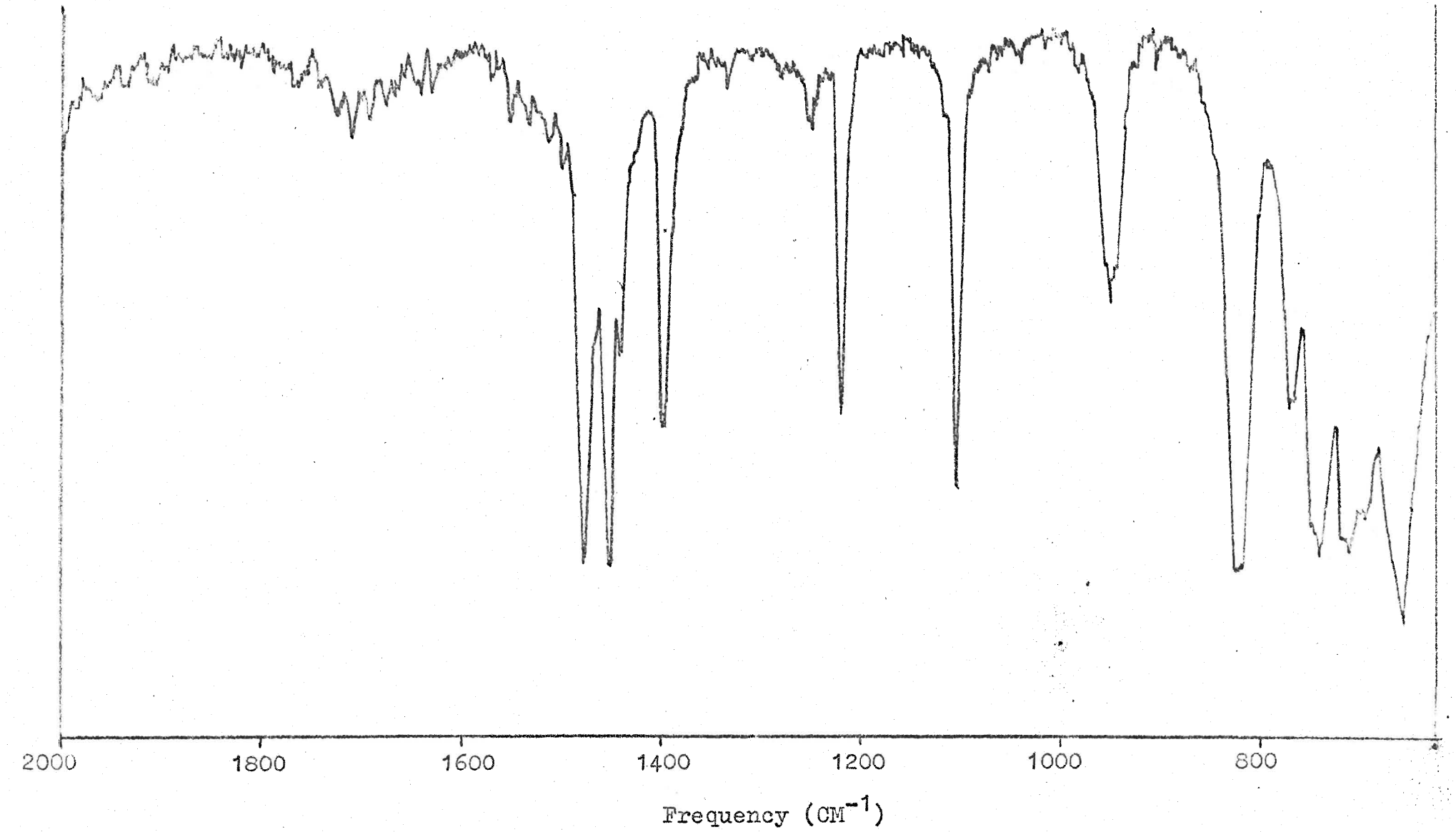

2000
1800
1600
1400
1200
1000
800
Frequency (CM-1)

TABLE 12 The Mass Spectrum of $(CH_3)_3NBClBr_2$

m/e	Intensity	% total ion current (a)	Proposed structure
254	0.39		
253	0.13		$BBr_3^{+\cdot}$ formed by rearrangement of parent, and loss of $(CH_3)_3N$.
252	1.21		
251	0.34	0.34	
250	1.21		
249	0.30		
248	0.39		
247	0.13		
233	0.26		
232	6.5		
231	2.4		
230	12.9	2.95	$(CH_3)_3NBBr_2^+$
229	4.3		
228	6.9		
227	2.2		
218	0.13		
217	0.22		
216	0.55		31.2% $(CH_3)_2NBBr_2^{+\cdot}$
215	0.62	0.33	and
214	1.17		68.8% $C_2H_5NBBr_2^+$
213	0.52		
212	0.55		
211	0.17		

m/e	Intensity	% total ion current	Proposed structure
210	3.0		
209	0.86		
208	15.1		
207	3.9		
206	19.4	4.95	$BClBr_2^{+\cdot}$
205	5.4		
204	9.5		
203	2.4		
189	1.3		
188	30.2		
187	11.2		
186	100.0	23.3	$(CH_3)_3NBClBr^+$
185	35.3		
184	80.6		
183	22.0		
173	8.2		
172	3.0		
171	16.2		63.7% BBr_2^+
170	11.9	5.03	and
169	9.1		36.3% $C_2H_5NBClBr^+$
168	9.5		
167	2.6		

m/e	Intensity	% total ion current	Proposed structure
164	3.0		
163	0.73		
162	6.9		
161	1.7	1.54	$BCl_2Br^{+\cdot}$
160	4.7		
159	1.1		
158	0.41		
154	0.5		
153	1.17		
152	1.7		52.66% $(CH_3)_3NBBr^{+\cdot}$
151	0.65	0.84	and.
150	2.6		47.34% $(CH_3)_3NBHBr^{+}$
149	4.3		
148	0.14		
142	3.0		
141	1.1	0.9	$(CH_3)_3NBCl_2^{+}$
140	5.2		
139	1.5		
136	9.9		
135	3.0	2.2	$(CH_3)_2NBBr^{+}$
134	10.3		
133	3.2		

m/e	Intensity	% total ion current	Proposed structure
130	0.17		
129	23.2		
128	6.7		92.22% $BClBr^+$, 2.38% $BHClBr^{+\cdot}$
127	87.9	19.27	and
126	24.6		5.40% $(CH_3)_2NBCl_2^{+\cdot}$
125	70.3		
124	19.0		
120	2.2		
119	0.69		
118	4.3	1.06	$BCl_3^{+\cdot}$
117	1.3		
116	3.4		
115	0.9		
109	0.38		
108	0.31		21.5% $(CH_3)_3NBCl^{+\cdot}$
107	2.6		19.7% $(CH_3)_3NBHCl^+$
106	1.5	0.91	and
105	3.0		58.8% $BBrNH^+$
104	2.2		
103	0.47		
102	0.5		

m/e	Intensity	% total ion current	Proposed structure
93	2.8		
92	13.8		97.16% $(CH_3)_2NBCl^+$
91	4.7	6.2	and
90	39.7		2.8% $BBr^{+\cdot}$
89	11.9		
88	1.7		
85	4.7		
84	1.3		
83	27.6		
82	37.9	15.69	Br^+ and HBr^+
81	44.8		
80	41.4		
79	31.0		
63	3.2		
62	1.9		
61	7.8		
60	4.3		
59	62.1	14.47	$(CH)_3N^{+\cdot}$ and $C_3H_8N^+$
58	65.5		
57	15.9		
56	6.5		
55	3.0		
54	3.9		

a: all figures represent the sum of polyisotopic contributions

TABLE 13 The Mass Spectral Analysis of the Decomposition of $(CH_3)_3NBBr_2X$

$(Ion)^+$	Ion Abundance (a) X = F(b)	X = Cl
$(CH_3)_3NBBr_2X$	0.2	-
$(CH_3)_3NBBr_2$	0.9	2.95
$(CH_3)_3NBBrX$	28.8	23.33
$(CH_3)_2NBBr$	0.3	2.20
$(CH_3)_3N^{\bullet}$ and C_3H_8N	9.9	14.47

(a) Ion abundances expressed as the percentage of total ion current. All figures represent the sum of polyisotopic contributions.

(b) Ref. 10.

from the table. $(CH_3)_3NBFBr_2$ forms a weak molecular ion whilst a parent could not be detected from the mono-chloro mixed adduct even when the ionizing voltage was reduced to 20 eV. The lower abundance of the ion $(CH_3)_3NBBr_2^+$ from $(CH_3)_3NBFBr_2$ compared with $(CH_3)_3NBClBr_2$ is consistent with earlier postulations (70) that as the molecular weight of the halogen increases the halogen-boron π-back bonding decreases, thus allowing the heavier halogen to be removed from the parent more easily. The most abundant ion in each case was formed by loss of a bromine atom from the parent ion. This is expected statistically; yet the abundance of the (parent - bromine)$^+$ ion may also be enhanced by the weaker residual π-bonding in the boron-bromine bonds as compared to B-Cl and B-F bonds. The data indicates loss of Br in preference to Cl, but Cl in preference to F.

The relative strength of the boron-nitrogen bond in the mixed adducts may be inferred from the abundances of the ions $C_3H_9N^{+\cdot}$ and $C_3H_8^+$. The data suggests that when the fluorine is replaced by chlorine the boron-nitrogen bond becomes stronger; that $BClBr_2$ is therefore a stronger donor than $BFBr_2$. This supports proton N.M.R. evidence which indicates that the acceptor strength of the boron halides progressively increases as halogens of higher molecular weight are substituted for lighter halogens.

However, care must be taken in concluding too much from such data as kinetic effects may also be important.

iv) Reverse reactions

Reverse reactions are the reactions between an adduct and a free boron trihalide containing a halogen of lower molecular weight. They were undertaken in an effort to determine whether the relative strengths of free and complexed Lewis acids are an important criterion in the halogen exchange mechanism.

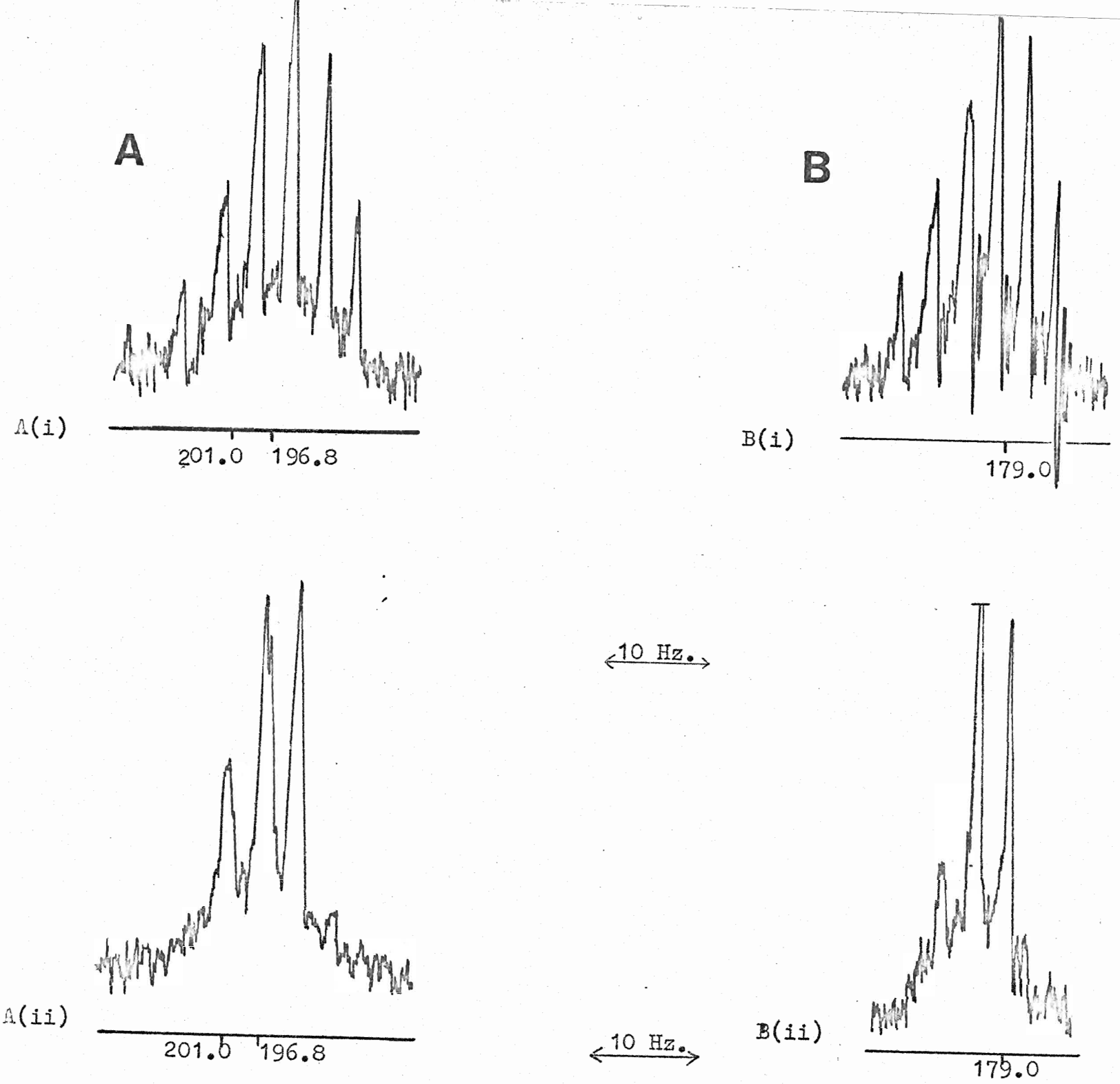
Initial qualitative attempts to study these reactions showed that $(CH_3)_3NBI_3$ reacted almost immediately with BBr_3 at ambient temperatures. The spectrum recorded after warming the sample to room temperature showed four overlapping quartets; the boron-11 decoupler simplified the spectrum to four singlets having chemical shifts corresponding to both mixed adducts and both parent trihalide adducts. Typical spectra are shown in Figure 9. Similar reactions showed that $(CH_3)_3NBI_3$ reacted slowly at room temperature with BCl_3, so that mixed adducts and $(CH_3)_3NBCl_3$ were present in the system after 24 hours; and to a very limited extent with BF_3 in that only a trace of $(CH_3)_3NBF_3$ could be detected after several days at 25°C. Heating the latter sample at 50°C did not affect the reaction at all. In view of their known stability, it is

FIGURE 9

^{1}H N.M.R. Spectra of:-

A) $(CH_3)_3NBI_3 + BBr_3$ (i) Normal
(ii) ^{11}B decoupled

B) $(CH_3)_3NBBr_3 + BCl_3$ (i) Normal
(ii) ^{11}B decoupled


A
A(i)
201.0
196.8
B
B(i)
179.0
10 Hz.
A(ii)
201.0
196.8
10 Hz.
B(ii)
179.0

not surprising that mixed fluoride/iodide complexes could not be seen in this sample. $(CH_3)_3NBBr_3$ was found to react at a moderate rate with BCl_3, but neither $(CH_3)_3NBBr_3$, nor $(CH_3)_3NBCl_3$ were found to react to any significant extent with BF_3, only a trace of $(CH_3)_3NBF_3$ being detected. It was naturally concluded that BF_3 was too weak a Lewis acid to displace bromine or chlorine from an adduct. However, a report by Krishnamurthy and Lappert (241), whilst supporting the results of the reactions $(CH_3)_3NBBr_3$ and BCl_3 and $(CH_3)_3NBCl_3$ and BF_3 found above, indicated that $(CH_3)_3NBBr_3$ and BF_3 (0.2M in each component) would react together to form mixed adducts.

To place any findings on a more quantitative basis, all reactions were repeated at concentrations of 0.2 molar in each component. The results essentially supported the data of the previous qualitative work; that $(CH_3)_3NBI_3$ reacted immediately with BBr_3, $(CH_3)_3NBI_3$ and $(CH_3)_3NBBr_3$ reacted more slowly with BCl_3 while other combinations of adducts and free boron halide gave results that were not conclusive.

In order to investigate these systems more carefully, it was decided to repeat some experiments at different relative concentrations, and with different components which it was thought might influence the reaction. To this end, the reactions listed in Table 14 were carried out.

TABLE 14 Samples Prepared to Investigate Some Reverse Reactions

	System	Relative Concentration(a)	Results
1	$DBI_3 + BF_3$ (b)	1 : 10	DBF_3 formed. No mixed adducts detected.
2	$DBBr_3 + BF_3$	1 : 10	Reaction forming mixed adducts
3	$DBCl_3 + BF_3$	1 : 10	Mixed adducts and DBF_3 formed.
4	$DBBr_3 + BF_3 + H_2O$	0.2M in each	No reaction.
5	$DBBr_3 + BF_3 +$ EtOH	0.2M in each	" "
6	$DBBr_3 + BF_3 + BBr_4^-$	0.2M in each	Insignificant amount of reaction.
7	$DBBr_3 + BF_3 + BF_4^-$	0.2M in each	" " "
8	$DBBr_3 + BF_3 +$ HBr	0.2M in each	" " "
9	$DBCl_3 + BF_3 + BCl_4^-$	0.2M in each	" " "
10	$DBCl_3 + BF_3 + BF_4^-$	0.2M in each	" " "

(a) Concentrations refer only to the adduct and boron trihalide. Concentrations of other components were not measured accurately.

(b) D = $(CH_3)_3N$.

Interesting results were obtained in the systems containing adduct and boron halide in a mole ratio of 1 : 10. $(CH_3)_3NBF_3$ was formed quickly in reaction 1 and after 24 hours at 50°C and several days at room temperature only this product was detected. N.M.R. signals corresponding to mixed fluoride/iodide adducts were not seen at all during the course of the reaction, but they were not really expected. After 24 hours at 50°C, all four possible adducts in reaction 2 (Figure 10A) were detected and the reaction continued slowly at ambient temperatures. This result supports the findings of Krishnamurthy and Lappert (241) that halogen exchange will occur in this system, but also suggests that some error may have been made in their measuring of concentrations. Under the same conditions required for the BBr_3 adduct to react, system 3 showed that halogen exchange would occur when $(CH_3)_3NBCl_3$ was mixed with BF_3 (Figure 10B).

A series of reactions 4-10 were carried out to see if catalysis were important. The spectra of reactions 4 and 5 showed no change with time, even when the samples were maintained at 50°C. Only one quartet, corresponding to $(CH_3)_3NBBr_3$ was seen. This may indicate that the BF_3 had complexed with the water or alcohol thus protecting the system. The addition of ionic species and HBr to the system (reactions 6-8) gave inconclusive results. In each

FIGURE 10

^{1}H N.M.R. Spectra of:-

A) $(CH_3)_3NBBr_3 + BF_3$ (1 : 10 mole ratio)

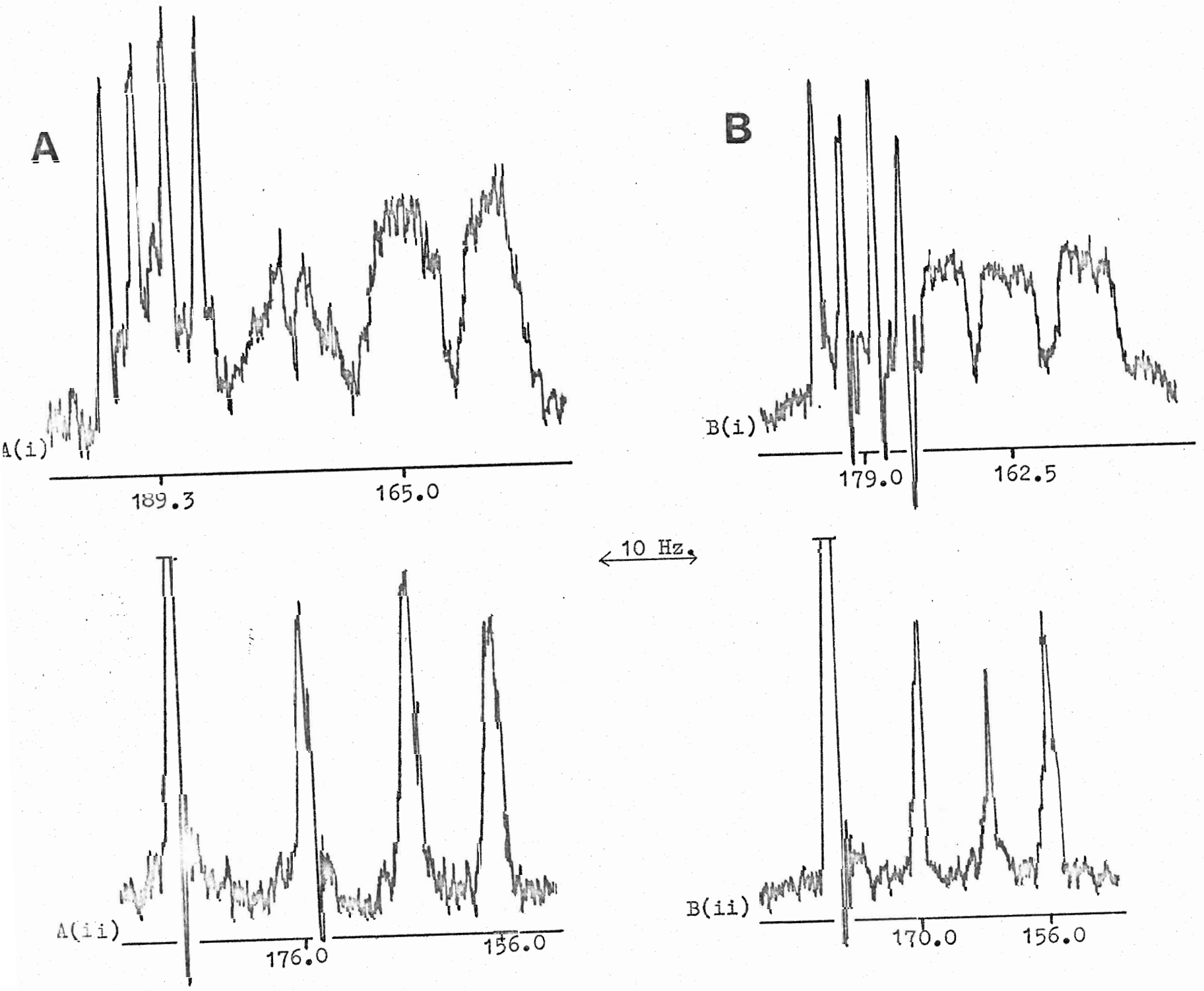
i) Normal

ii) ^{11}B decoupled

B) $(CH_3)_3NBCl_3 + BF_3$ (1 : 10 mole ratio)

i) Normal

ii) ^{11}B decoupled


A
A(i)
189.3
165.0
B
B(i)
179.0
162.5
10 Hz
A(ii)
176.0
156.0
B(ii)
170.0
156.0

case only a trace of $(CH_3)_3NBF_3$ and $(CH_3)_3NBFBr_2$ could be detected after several days. Since insignificant amounts of products were noted in the initial reaction of $(CH_3)_3NBBr_3$ and BF_3 (0.2M in each component) it seems probable that tetrahaloborate ions and HBr do not promote halogen exchange.

Analogous reactions (9 and 10) using $(CH_3)_3NBCl_3$ yielded similar results.

v) Reverse reactions using labelled adducts

Having established that reverse reactions would occur, the next logical step seemed to be an investigation to determine whether or not the B-N bond remained intact during such halogen exchange. Boron-10 labelled adducts were used for this purpose. Typical results are presented in Figure 11, which shows the spectra recorded from the systems $(CH_3)_3N^{10}BI_3/BBr_3$ and $(CH_3)_3N^{10}BI_3/BCl_3$; in each case the boron trihalide contains natural abundance boron. Examination of the spectra reveals that halogen exchange has occurred, while the absence of the characteristic 1 : 1 : 1 : 1 quartet, in favour of the seven-line multiplet clearly indicated that the reaction has proceeded without rupture of the boron-nitrogen bond. Identical results were recorded for the other combinations of adduct and free trihalide. Worthy of note was the system containing

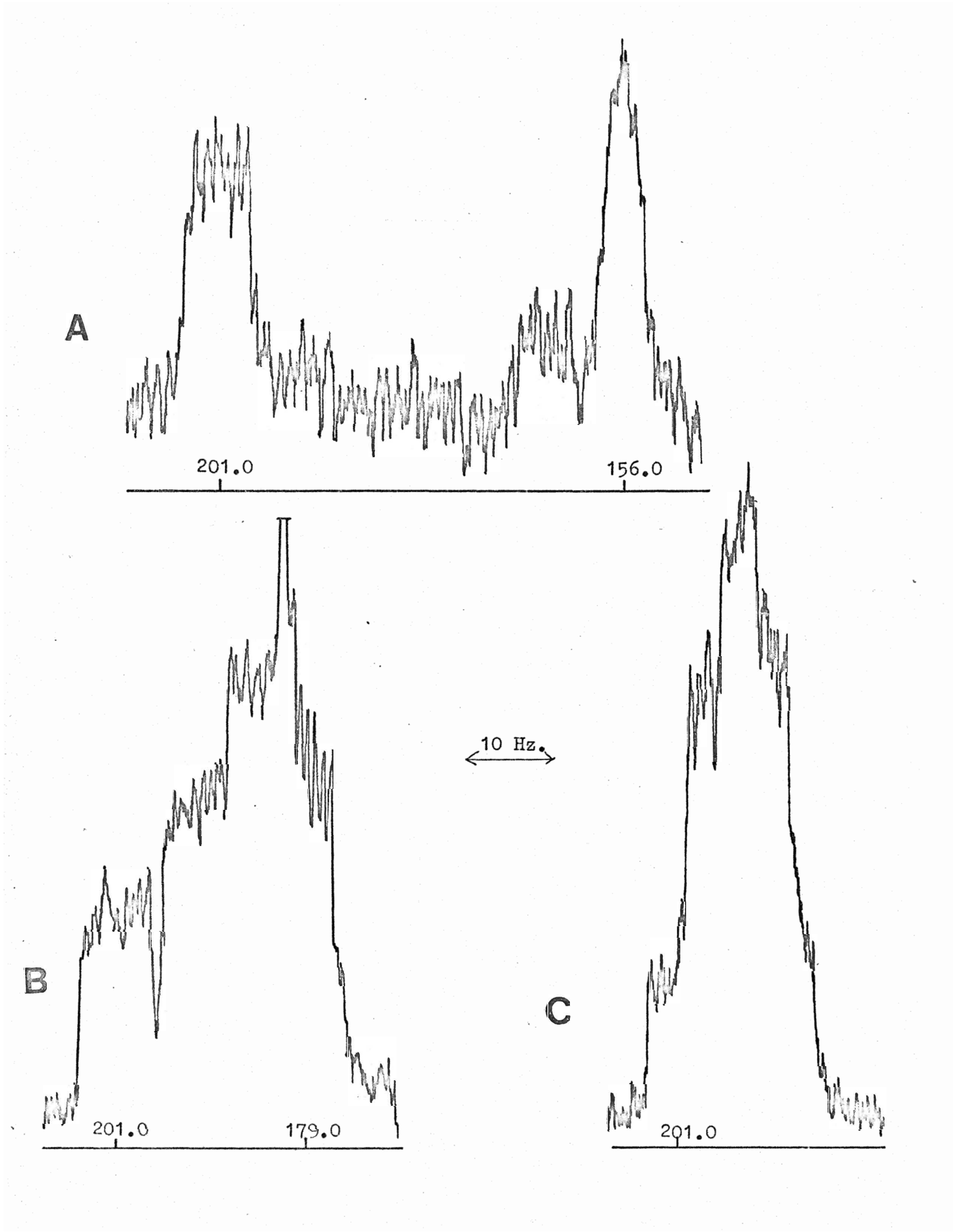
FIGURE 11

^{1}H N.M.R. Spectra of:-

A) $(CH_3)_3N^{10}BI_3 + BF_3$ (1 : 10 mole ratio)

B) $(CH_3)_3N^{10}BI_3 + BCl_3$ (0.2M in each)

C) $(CH_3)_3N^{10}BI_3 + BBr_3$ (0.2M in each)


A
201.0
156.0
B
201.0
179.0
10 Hz
C
201.0

$(CH_3)_3N^{10}BI_3$ and BF_3 in a mole ratio of 1 : 10. Although exchange was expected, and did indeed occur, the identification of a peak corresponding to $(CH_3)_3N^{10}BF_2I$ (Figure 11) was somewhat unexpected; during the previous reverse reaction on this system, using isotopically natural boron, neither mixed adduct was detected.

b) Gas Phase Reactions

As a possible means to compare reaction mechanisms, it was decided that gas phase reactions might provide some interesting data. These types of reactions have previously been investigated by Dutton et al (185) and Coyle (186). The former workers measured the amount of BF_3 displaced from $(CH_3)_3NBF_3$ after its reaction with free BCl_3 at different temperatures. They proposed that at temperatures below 150°C, displacement of the boron trifluoride probably resulted from the bimolecular interaction of BCl_3 with the adduct. At 205°C, however, partial dissociation of the adduct was believed to be more important. This postulate was later supported by Coyle (186) who used radioisotopic dilution techniques to establish that displacement of BF_3 from Et_3NBF_3 by BCl_3 occurred by two different pathways. Under mild conditions it became apparent that exchange of boron atoms bonded to the donor atom was not important; at 60°C boron-nitrogen bonds were cleaved as

evidenced by the nearly complete isotopic equilibration of the boron in the system.

During the course of this investigation, labelled adducts and a boron trihalide (containing natural abundance boron) in a mole ratio of 5 : 2, were sealed into an evacuated glass tube. The samples prepared are listed in Table 15. The spectra recorded immediately after the desired reaction time showed in all cases that halogen exchange had been effected. Figure 12 shows typical results. The complex overlapping resonances indicate that not only are the mixed adducts present, but also that boron-11 has been incorporated into the adduct. Thus dissociation of the donor and acceptor must have occurred. The only system in which mixed adducts were absent was the fluoride/iodide system.

Interesting results were obtained from reactions 18 and 19 -- the reverse gas phase systems in which BF_3 was the free trihalide. In each case the extent of halogen exchange was much reduced, (Figure 12), compared to the forward reactions. Yet isotopic equilibration had occurred within the system as evidenced by the proportion of boron-11 bound in the adduct. This may be interpreted in terms of the relative Lewis acidity of the boron trihalides and shows that BF_3 is considerably weaker than BCl_3 and BBr_3.

TABLE 15 Samples Used in Gas Phase Reactions

Reaction Number	System (a)	Products
11	$(CH_3)_3N^{10}BF_3$ + BCl_3 (b)	Mixed adducts (c)
12	$(CH_3)_3N^{10}BF_3$ + BBr_3	Mixed adducts
13	$(CH_3)_3N^{10}BF_3$ + BI_3	Mixed adducts
14	$(CH_3)_3N^{10}BCl_3$ + BBr_3	Mixed adducts
15	$(CH_3)_3N^{10}BCl_3$ + BI_3	Mixed adducts
16	$(CH_3)_3N^{10}BBr_3$ + BI_3	Mixed adducts
17	$(CH_3)_3N^{10}BBr_3$ + BCl_3	Mixed adducts
18	$(CH_3)_3N^{10}BBr_3$ + BF_3	Mixed adducts
19	$(CH_3)_3N^{10}BCl_3$ + BF_3	Mixed adducts

(a) All concentrations were the same; namely an adduct-acid ratio of 5 : 2.

(b) The free boron trihalides contained natural abundance boron.

(c) The mixed adducts contained both isotopes of boron.

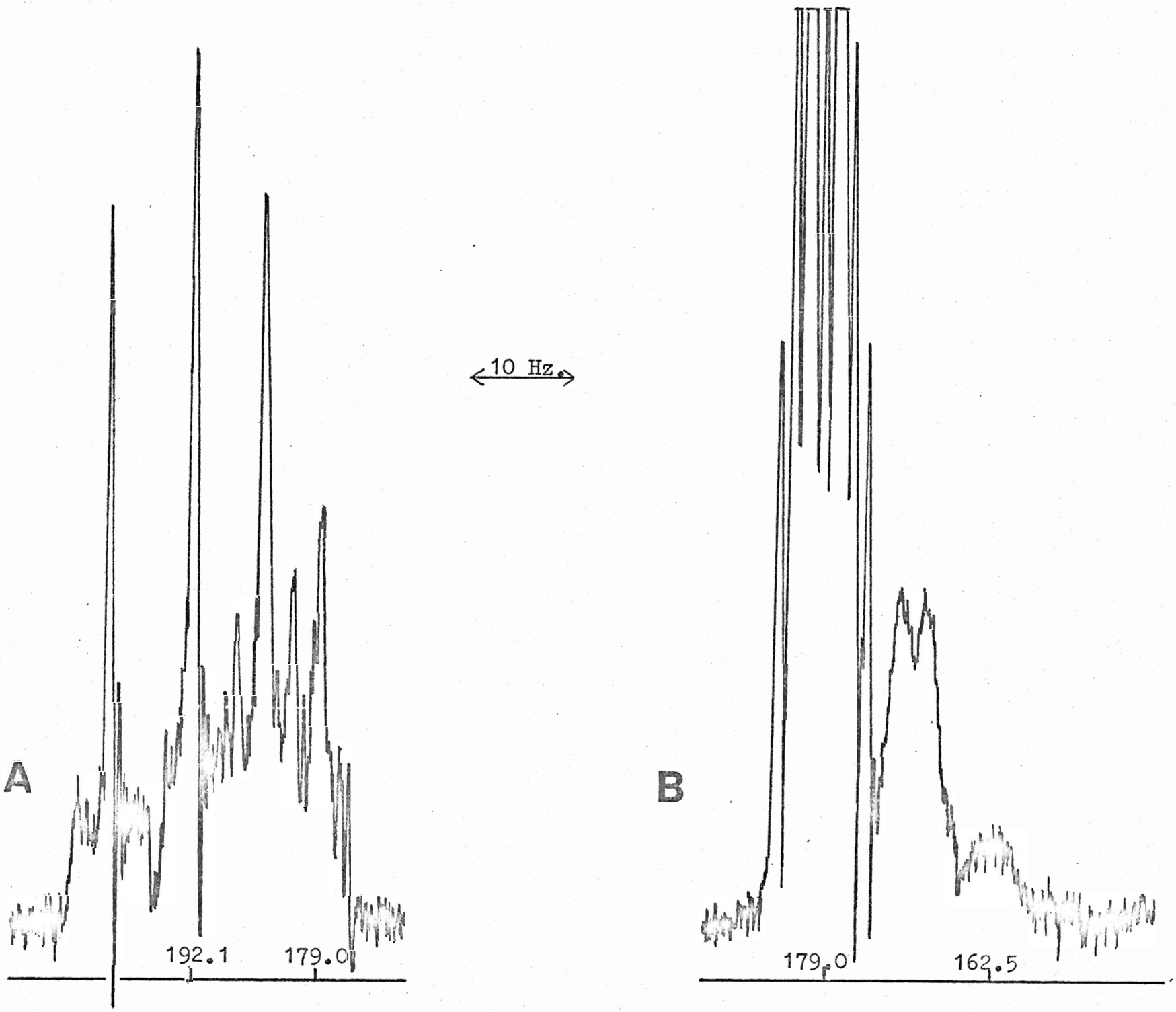
FIGURE 12

^{1}H N.M.R. Spectra of:-

A) $(CH_3)_3N^{10}BCl_3 + BI_3$ (^{11}B decoupled)

B) $(CH_3)_3N^{10}BCl_3 + BF_3$

After heating for 3 hours at 160°C in the gas phase.


10 Hz
A
192.1
179.0
B
179.0
162.5

B. THE REACTIONS OF ADDUCTS WITH SOME ANHYDROUS METAL CHLORIDES

i) Aluminium Trichloride

The addition of a solution of aluminium chloride in methylene chloride to $(CH_3)_3NBF_3$ solution at room temperature caused a shoulder to appear on the downfield side of the adduct resonance. The shoulder sharpened to become a separate peak on decoupling and its chemical shift was measured at 162.0 Hz, thus indicating it to be $(CH_3)_3NBF_2Cl$. Further additions of the Lewis acid eventually resulted in the identification of $(CH_3)_3NBFCl_2$ and $(CH_3)_3NBCl_3$ (Figure 13) the relative concentrations of the four adducts altering with each addition.

Analogous reactions of aluminium trichloride with $(CH_3)_3NBBr_3$ and $(CH_3)_3NBI_3$ showed in each case that halogen exchange reactions proceeded rapidly at 25°C to form both mixed adducts and $(CH_3)_3NBCl_3$.

ii) Silicon Tetrachloride

Halogen exchange did not occur to any great extent when $(CH_3)_3NBF_3$ was allowed to react with silicon tetrachloride. After heating at 50°C followed by several days at ambient temperatures, only very small amounts of products could be detected. No reaction occurred between $(CH_3)_3NBBr_3$ and $SiCl_4$, but when $(CH_3)_3NBI_3$ was the adduct used, the

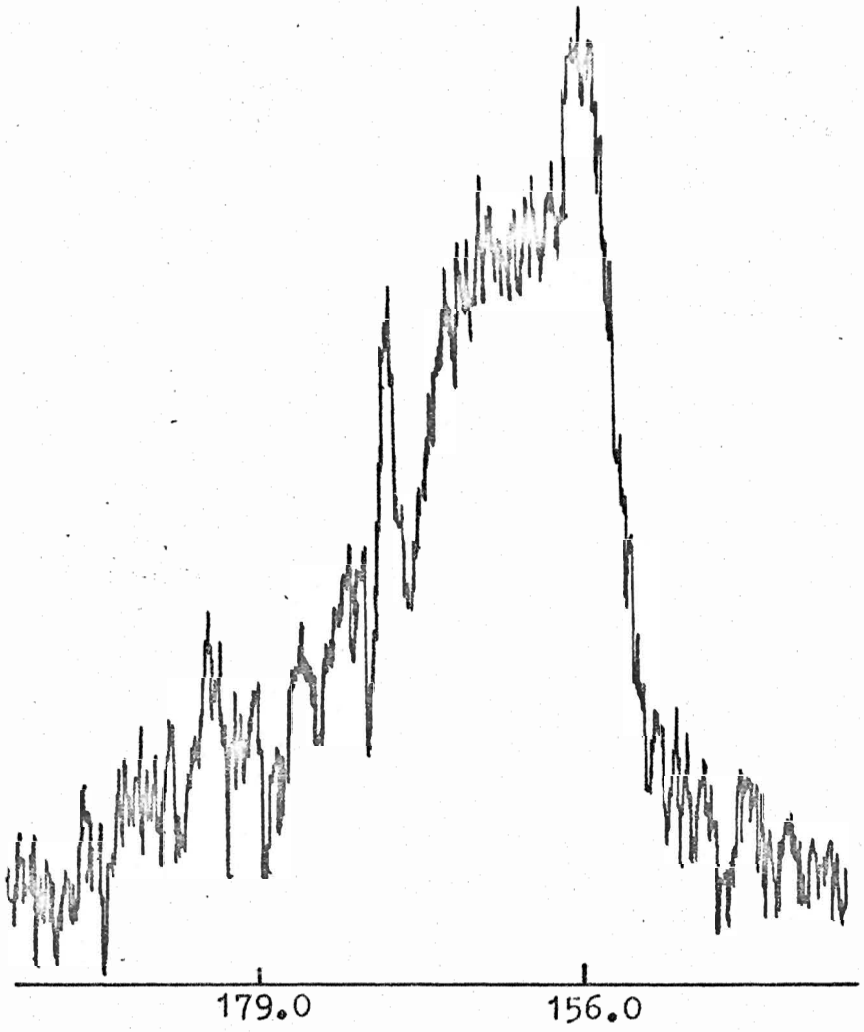
FIGURE 13

^{1}H N.M.R. Spectrum of $(CH_3)_3NBF_3 + AlCl_3$

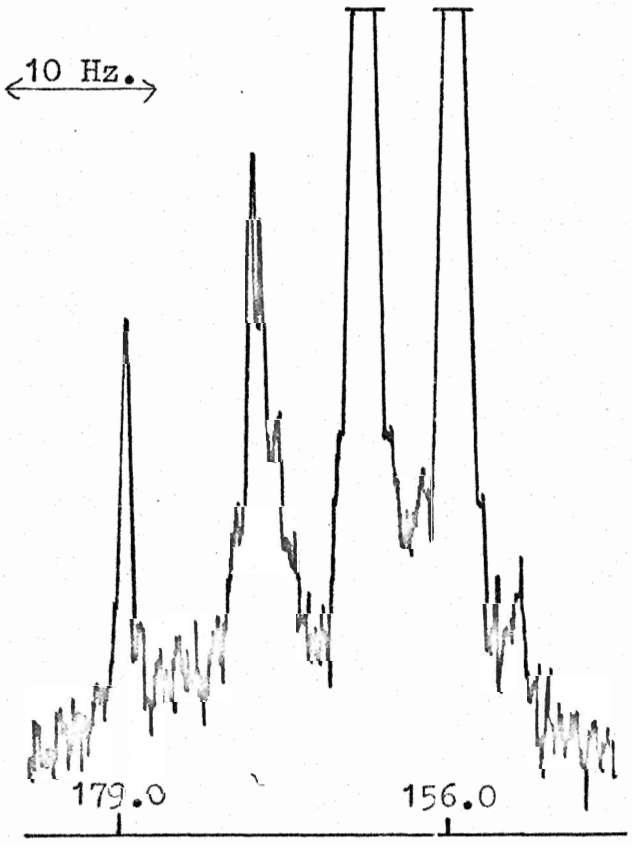
i) Normal

ii) ^{11}B decoupled

(i)



(ii)



solution turned brown after several days indicating that iodine was being displaced. The N.M.R. spectrum confirmed that halogen exchange had occurred by showing the resonances of $(CH_3)_3NBClI_2$ and $(CH_3)_3NBCl_3$. It is worth noting that $(CH_3)_3NBCl_2I$ could not be confidently detected in this system. The discrimination toward this adduct during the reaction is perhaps significant and may well be a reflection of the mechanism involved. Such an interpretation will be dealt with later in the discussion.

iii) Arsenic Trichloride

The lack of products after several days under the usual conditions showed that arsenic trichloride was not reacting with either $(CH_3)_3NBF_3$ or $(CH_3)_3NBBr_3$. A little decomposition occurred in each case, particularly the former in which a white crystalline precipitate formed in the tube. This may have been $(CH_3)_3NH^+Cl^-$ which was also identified by its characteristic doublet (J = 5.0 Hz) in the spectrum.

The system containing $(CH_3)_3NBI_3$ and arsenic trichloride also produced a thick white crystalline precipitate. But the solution turned yellow after 30 hours at 25°C indicating the displacement of iodine. This suggestion of halogen exchange was borne out by examination of the spectrum which revealed that the concentration of

$(CH_3)_3NBI_3$ had decreased. The presence of $(CH_3)_3NBClI_2$ was seen and the familiar quartet of the trichloride complex was easily recognized. Again the concentration of $(CH_3)_3NBCl_2I$ was unusually low, the resonance being barely detectable. The reaction continued slowly at room temperature until only $(CH_3)_3NBCl_3$ was present. An orange hexagonal crystal formed inside the N.M.R. tube. This was probably arsenic triiodide.

iv) Phosphorus Trichloride

Phosphorus trichloride was added to a solution of $(CH_3)_3NBX_3$ (X = F, Br and I). No halogen exchange products were detected after heating the samples for 24 hours at 50°C, and maintaining them at room temperature for several days.

v) Phosphorus Pentachloride

$(CH_3)_3NBF_3$ reacted slowly at 50°C with phosphorus pentachloride. After 24 hours all four adducts could be detected in the system. An interesting result was obtained from the mixture containing $(CH_3)_3NBBr_3$. No reaction was observed after several weeks at room temperature or when phosphorus pentachloride was present in a large excess.

Upon addition of phosphorus pentachloride to $(CH_3)_3NBI_3$ solution, the crystals dissolved and a purple

colour developed indicating the immediate displacement of iodine. A quartet corresponding to $(CH_3)_3NBCl_3$ was present in the spectrum recorded immediately after the addition. Further amounts of the pentachloride caused the relative peak areas to vary as the reaction proceeded. It is worth noting that in this system, as in the reaction of the boron trifluoride adduct with phosphorus pentachloride, the mixed adducts, although detected, were formed only in minute amounts (Figure 14).

C. REACTIONS OF ADDUCTS WITH ADDUCTS

i) Solution Reactions

Previous studies on these systems by Hartman and Miller (239) showed that $(CH_3)_3NBF_3$ and $(CH_3)_3NBCl_3$ by themselves were remarkably stable and did not undergo halogen exchange even when heated to 180°C. Their work was extended by preparing the samples listed in Table 16. Approximately equimolar amounts of two selected adducts were dissolved and the N.M.R. tubes were heated for several hours at 50°C (CH_2Cl_2), 70°C ($CHCl_3$) or 100°C (C_6H_5Cl) depending on the solvent chosen. Following that, they were allowed to stand for several days at 25°C. For interesting comparison, free trimethylamine was added to some samples. Halogen exchange in the presence of excess base has been documented (237) for the boron

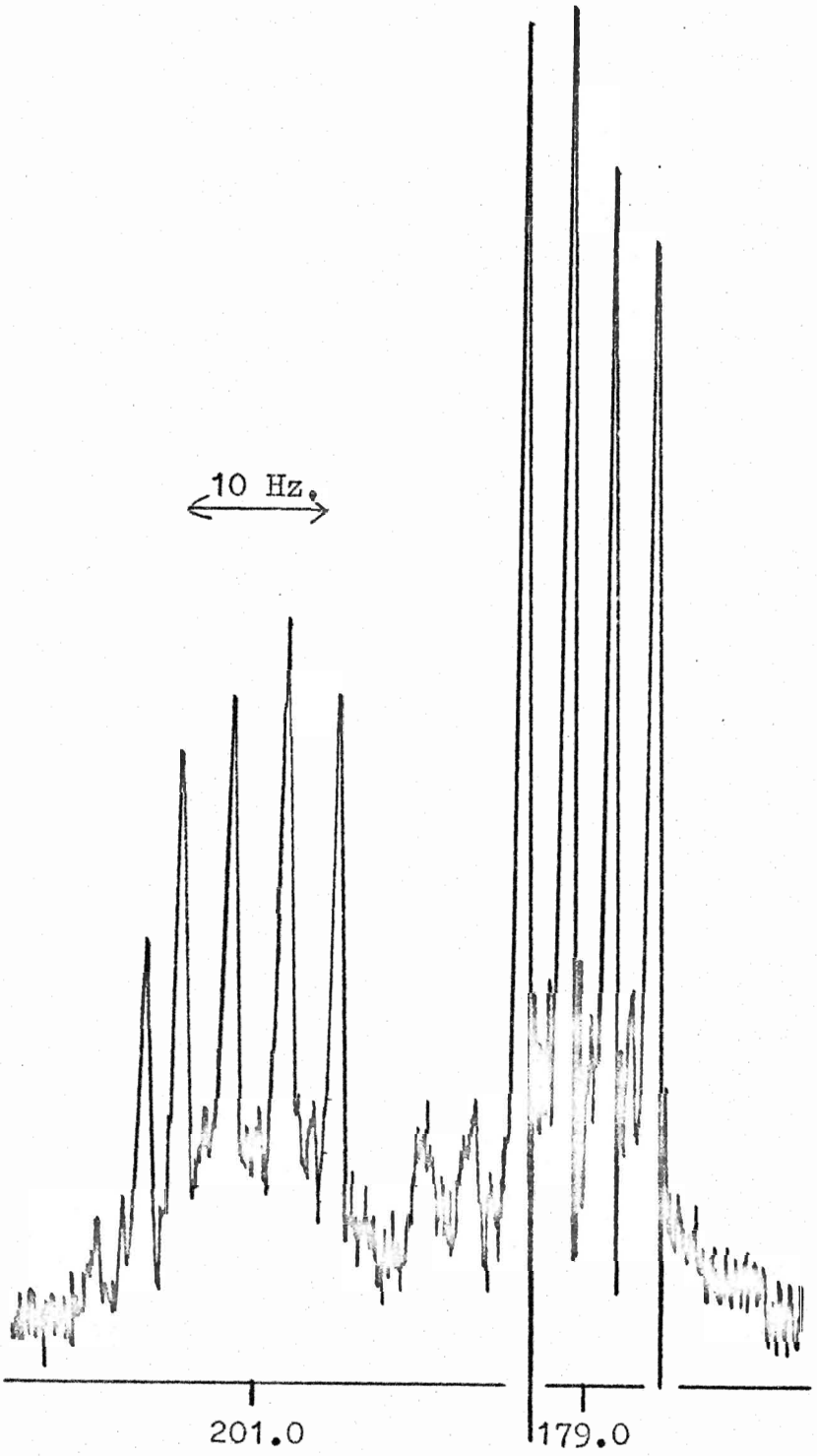
TABLE 16 Samples Prepared for Adduct Solution Reactions

Reaction Number	System	Solvent	Results
19	DBF_3 + $DBCl_3$ [(a)]	$CHCl_3$	No reaction
20	DBF_3 + $DBCl_3$ + D	$CHCl_3$	No reaction
21	DBF_3 + $DBCl_3$	C_6H_5Cl	No reaction
22	DBF_3 + $DBCl_3$ + D	C_6H_5Cl	No reaction
23	DBF_3 + DBI_3	CH_2Cl_2	No reaction
24	$DBCl_3$ + $DBBr_3$ + D	$CHCl_3$	No reaction
25	$DBCl_3$ + DBI_3	$CHCl_3$	No reaction
26	$DBBr_3$ + DBI_3	CH_2Cl_2	No reaction
27	$DBBr_3$ + DBI_3 + D	$CHCl_3$	No reaction

(a) D = $(CH_3)_3N$.

FIGURE 14

^{1}H N.M.R. Spectrum of $(CH_3)_3NBI_3$ + PCl_5


10 Hz.
201.0
179.0

trihalide complexes of dimethyl ether and it was felt that analogous reactions using trimethylamine as the donor might also yield some valuable results. Results, however, were very disappointing. In no case was halogen exchange effected. Decomposition occurred to a certain extent in all samples when they were heated. This was evidenced by the formation of a crystalline white precipitate, and various new resonances in the spectrum. The latter were not identified. The precipitate was believed to be protonated trimethylamine, recognized by the characteristic doublet, the chemical shift of which varied depending on the system being recorded. The precipitate was present to such an extent in some samples that it was necessary to transfer the contents to a new tube using a dropping pipette covered with glass wool. The decomposition was accompanied by a decrease in the intensity of the adduct resonances; this was particularly true for $(CH_3)_3NBF_3$. Allowing the samples to stand at room temperature did not alter the spectra at all. Indeed sample 26, which was used as a tuning sample for the heteronuclear decoupler, showed no appreciable decomposition after two years at that temperature.

ii) Gas Phase Reactions

The lack of results from the above reactions prompted an investigation into the possibility that

scrambling might occur when binary mixtures of the adducts were heated together in the absence of a solvent. Considering the published results of other workers (185, 186, 253), it seemed likely that dissociation of the adduct in the gas phase would precede halogen exchange.

Typically 0.5 millimoles of each adduct were sealed into an evacuated glass tube and heated for three hours. The temperature chosen initially, 300°C, was found to be too high since it caused extensive decomposition, particularly in the adducts containing halogens of higher molecular weight. Pure $(CH_3)_3NBBr_3$ decomposed into an oily reddish liquid, the N.M.R. spectrum of which revealed no trace of the starting material. Iodine and methyl iodide were among the decomposition products of the triiodide adduct. Accordingly the reaction temperature was reduced to 160°C; the spectra of the pure adducts after being heated at this temperature showed their normal resonances with only a minimum of breakdown products. Similarly, little decomposition had occurred in mixtures of two adducts, the only products of the type detected regularly being $(CH_3)_3NH^+$ and CH_3X (X = Br and I). However the spectra also showed that halogen scrambling had allowed formation of both mixed adducts. Figure 15 shows a sample spectrum; that of $(CH_3)_3NBCl_3$ and $(CH_3)_3NBBr_3$ after being heated.

FIGURE 15

^{1}H N.M.R. Spectra of:-

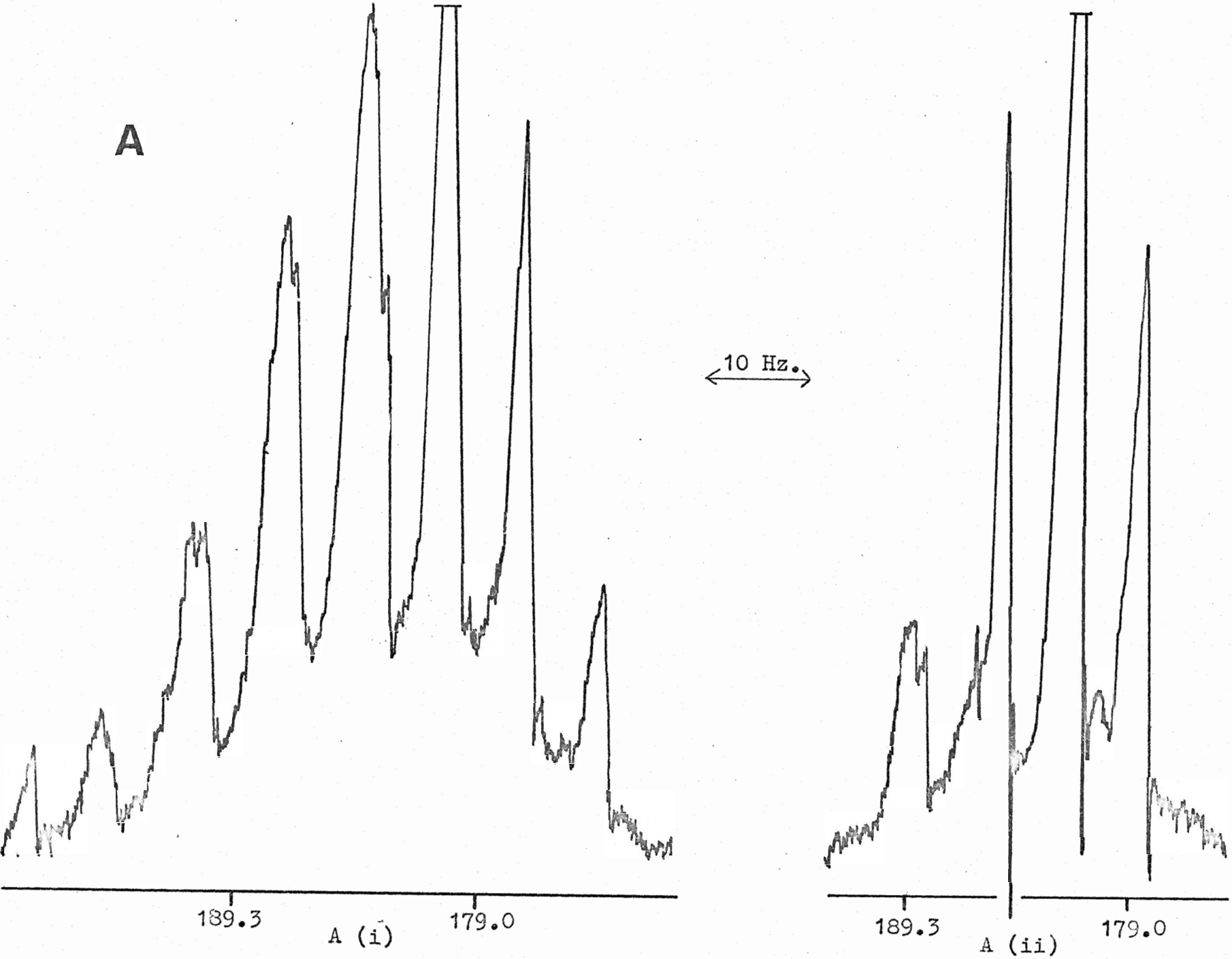
A) $(CH_3)_3NBCl_3 + (CH_3)_3NBBr_3$ i) Normal

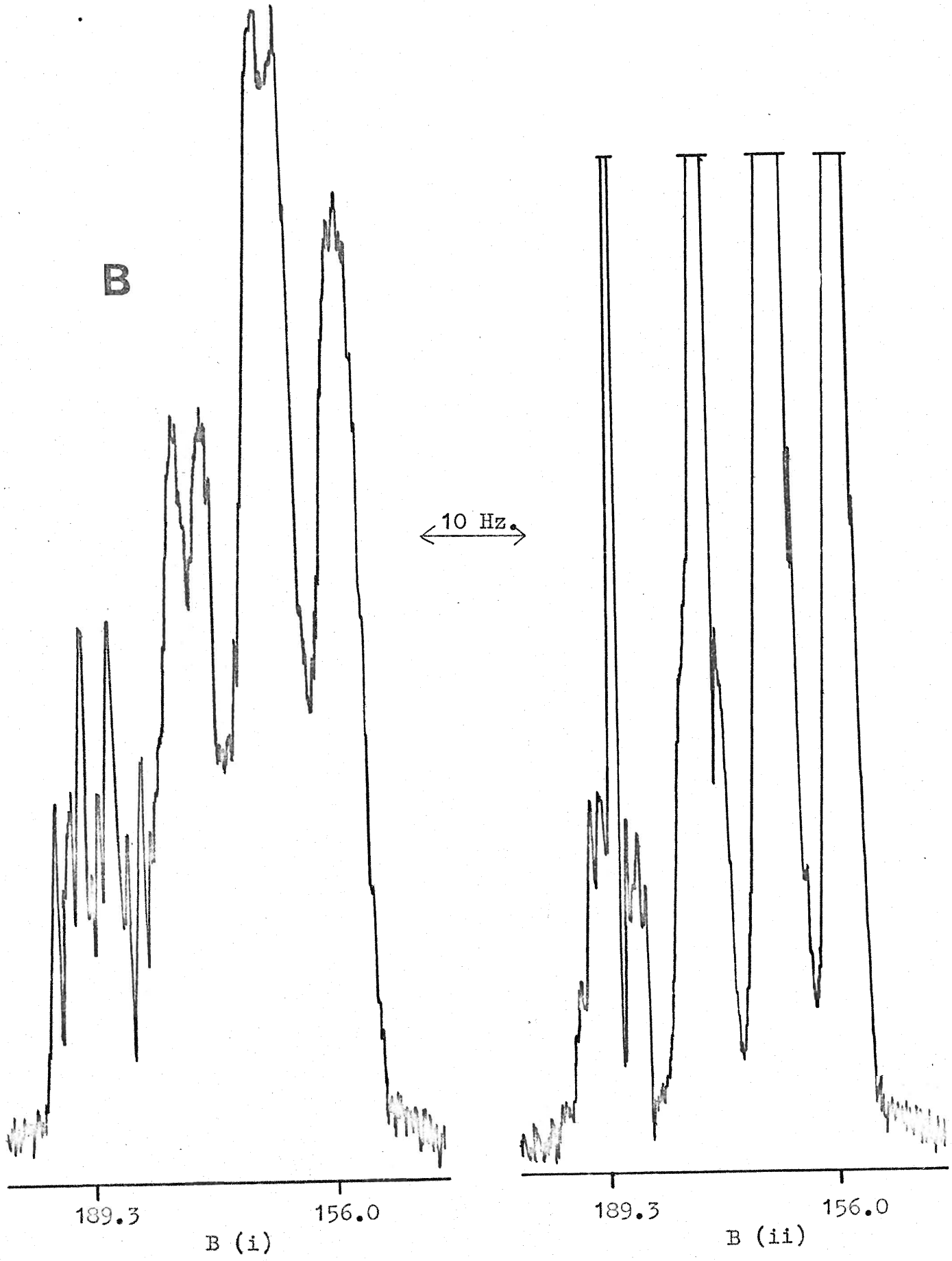
ii) ^{11}B decoupled

B) $(CH_3)_3N^{10}BF_3 + (CH_3)_3NBBr_3$ i) normal

ii) ^{11}B decoupled

after heating at 160°C for 3 hours


A
10 Hz.
189.3
179.0
A (i)
189.3
179.0
A (ii)


B
10 Hz
189.3
156.0
B (i)
189.3
156.0
B (ii)

Extension of this experiment showed complete equilibration of both boron isotopes throughout the products when one of the adducts used was enriched with boron-10. This is clearly shown in Figure 15.

D. THE REACTIONS OF ADDUCTS WITH HYDROGEN HALIDES

The data listed in Table 17 shows the various combinations of adducts and hydrogen halides that were prepared, and the different concentrations used in each case. Since some of the reverse reactions of adducts with free boron halides had already been shown to proceed only when a large excess of the Lewis acid was present, it was felt that such conditions might have been desired in these systems. Thus the samples incorporating an adduct : HX ratio of 1 : 10 were prepared. A trace of water to encourage ionization of the hydrogen halide was added to other samples in order to determine whether the presence of halide ions was of any significance in facilitating halogen exchange.

The results for all reactions, except those starting with $(CH_3)_3NBI_3$ were disappointing in that none of the products sought could be detected. Reactions occurring seem limited mainly to decomposition as evidenced by the formation of a crystalline precipitate -- e.g. $(CH_3)_3NH^+Cl^-$, recognized by its characteristic N.M.R.

TABLE 17 MIXTURES OF ADDUCTS AND HYDROGEN HALIDES

Adduct	Hydrogen Halide	Concentrations used	Results
DBF_3(i)	HCl	a) 0.2M[ii] b) 1 : 10 mole ratio[iii]	0[v]
DBF_3	HBr	a) 0.2M b) 1 : 10 mole ratio	0
DBF_3	HI	a) 0.2M b) 1 : 10 mole ratio c) 0.2M (H_2O)[iv]	0
$DBCl_3$	HBr	a) 0.2M b) 1 : 10 mole ratio	0
$DBCl_3$	HI	a) 0.2M b) 1 : 10 mole ratio c) 0.2M (H_2O)	0
$DBBr_3$	HI	a) 0.2M b) 1 : 10 mole ratio c) 0.2M (H_2O)	0
$DBBr_3$	HCl	a) 0.2M b) 1 : 10 mole ratio c) 0.2M (H_2O)	0
DBI_3	HBr	a) 0.2M b) 1 : 10 mole ratio c) 0.2M (H_2O)	+[vi]
DBI_3	HCl	a) 0.2M b) 1 : 10 mole ratio c) 0.2M (H_2O)	+

---

i) D = $(CH_3)_3N$

ii) Means 0.2M in each component

iii) The adduct : hydrogen halide mole ratio was 1 : 10.

iv) The principal constituents were 0.2M. A trace of water was added to the system.

v) 0: Means no reaction occurred.

vi) +: Means reaction occurred and mixed adducts were formed.

resonance -- in most samples, and the presence of a faint yellow colour in those samples containing hydrogen iodide. The triiodide complex yielded more interesting data. This adduct reacted very slowly with hydrogen bromide when both components were anhydrous and the concentrations of each were 0.2M. Slight yellowing of the solution occurred with the formation of the familiar precipitate inside the tube. Analysis of the sample showed that exchange had occurred and allowed identification of $(CH_3)_3NBBrI_2$ at 196.5 Hz. The sample containing the large excess of hydrogen bromide had undergone more changes than the previous system, thus allowing identification of all four adducts after heating the tube at 50°C for 24 hours. The presence of water in the third mixture encouraged the formation of a gelatinous precipitate inside the N.M.R. tube. The appearance of a yellow colour after 1 day at ambient temperature suggested that halogen exchange was occurring, but more substantial evidence of any reaction was not found by recording the spectrum. After heating the system, however, both mixed adducts were found to be present as was $(CH_3)_3NBBr_3$. The most significant fact about these results was that the halogen exchange reaction had proceeded to a greater degree in this system than in the analogous anhydrous one (Figure 16). The importance of the effect of water

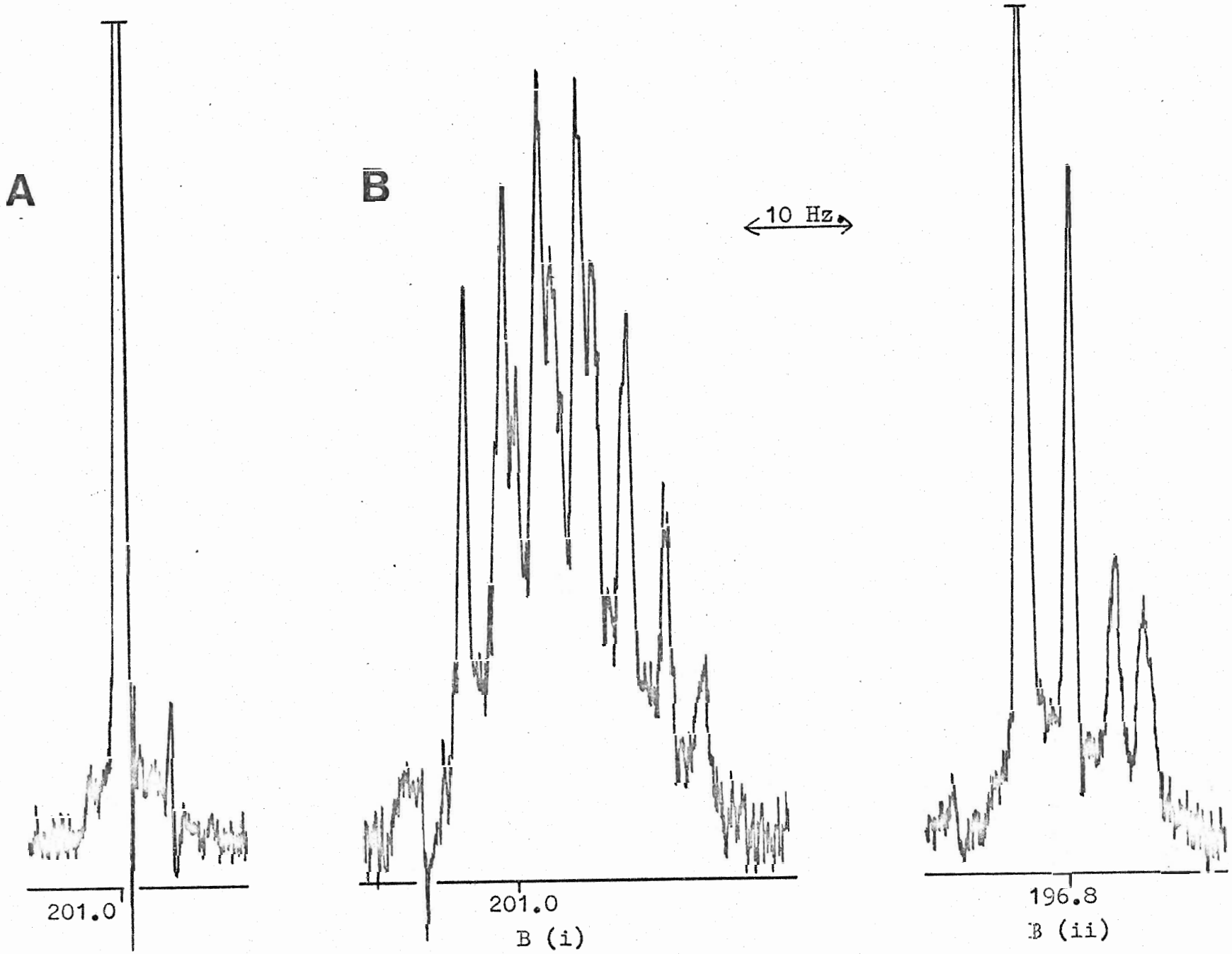
FIGURE 16

^{1}H N.M.R. Spectra of:-

A) $(CH_3)_3NBI_3$ + HBr (0.2M in each) ^{11}B decoupled

B) $(CH_3)_3NBI_3$ + HBr + H_2O i) Normal

ii) ^{11}B decoupled


A
B
10 Hz
201.0
201.0
B (i)
196.8
B (ii)

on the mechanism of halogen exchange, in encouraging ionization of the hydrogen halide is thus clearly established for the triiodide adduct.

E. THE REACTIONS OF ADDUCTS WITH IONIC SPECIES

Ionization of the adducts has to be considered as a plausible mechanism for halogen exchange, and the need for a systematic investigation into this possibility can thus be appreciated. To this end it was decided to mix the adducts with ionic compounds that might encourage halogen exchange. Tetraalkylammonium salts are admirably suited to such a purpose. Samples prepared included all possible combinations of Me_3NBX_3 (X = F, Cl, Br and I) with the following tetraalkylammonium salts; $Et_4^+NA^-$ ($A^- = F^-$, Cl^-, BF_4^-, BCl_4^-, OAc^-, NO_3^- and BH_4^-); and $Bu^n_4N^+B^-$ ($B = Br^-$, I^- and BBr_4^-). Exceptions were those samples in which the halogen atoms of the salt and adduct were the same and the samples that would contain Me_3NBI_3 with NO_3^- and BH_4^-. The acetate, nitrate and borohydride salts were included in an effort to obtain, for the first time, mixed adducts in which the groups bonded to the boron were not exclusively halogen atoms.

There are several general spectral features of the tetraethylammonium cation that are worthy of note. Considering $Et_4N^+Cl^-$ as an example -- the chemical shifts

of others were found to vary slightly depending on the system -- the methyl group absorbs as a basic 1 : 2 : 1 triplet centred at 83 Hz (1.38δ) $J1_{H-}{}^{1}_{H}$ = 7.5 Hz. Each of the three triplet peaks is further split into three smaller peaks in a 1 : 1 : 1 ratio ($J1_{H-}{}^{14}_{N}$ = 1.5 Hz). This is caused by coupling of the methyl protons to nitrogen-14 (I = 1), thus indicating a symmetrical environment. The methylene group resonates at 211 Hz (3.51δ) as a quartet (coupled to the methyl protons), but no coupling with nitrogen is apparent. The proton resonances of $Bu^{n}_{4}N^{+}$ occur in those regions of the spectrum expected for saturated hydrocarbons, with little discernable fine structure. The low field peaks formed a broad patch from about 215-185 Hz and as such might have interfered, in some cases, with the detection of any products. This was particularly true when labelled adducts were used; peaks of adducts containing natural abundance boron could be sharpened substantially by use of the heteronuclear decoupler.

The results generally showed that excepting $(CH_3)_3NBI_3$, adducts would not react with the ionic salts to give mixed adducts. Two extra systems were prepared for interest's sake; they were $(CH_3)_3NBF_3$ with Cl^- and BCl^-_4, each containing excess trimethylamine. The free base did not seem to have any noticeable effect, other than

to account for the production of a little $(CH_3)_3NBCl_3$ in the mixture containing $Et_4N^+BCl_4^-$. Therefore free base was not included in any other systems. Partial decomposition of $(CH_3)_3NBF_3$ was evident in most cases, particularly when OAc^- was present. In the latter example, this led to a confusing array of new peaks in the spectrum and the production of a few drops of a colourless oil, immiscible with the solvent. Decoupling suggested the absence of boron and the peaks were unassigned. The BH_4^- ion absorbed as a 1 : 1 : 1 : 1 quartet centred 10.5 Hz above T.M.S. ($J1_{H-}11_B$ = 82 Hz). The quartet could be collapsed by double irradiation but no singlet replaced the resonance when this was done in noise decoupling mode, presumably due to lack of power. During the course of the reaction, the intensity of the quartet diminished considerably indicating the rapid decomposition of $Et_4N^+BH_4^-$.

Halogen exchange reactions were noticed when the boron triiodide complex was used. After maintaining the sample containing this adduct and $Et_4N^+BCl_4^-$ at 50°C for 48 hours, $(CH_3)_3NBCl_3$ could be clearly identified (Figure 17) as could $(CH_3)_3NBClI_2$; the spectrum showed a conspicuous lack of the other mixed adduct. Almost identical results were noted for the sample containing $Et_4N^+Cl^-$. In other combinations, $(CH_3)_3NBBrI_2$ was detected

in the presence of $Bu^n_4N^+Br^-$ whilst there was no real evidence of exchange when BBr_4^- was the bromine containing entity. Conclusions are difficult to draw in this last case. The lack of evidence may arise merely because the resonance of the butyl group obscures the area of interest. None of the desired products could be detected when $(CH_3)_3NBI_3$ was mixed with F^-, but a yellow solution was seen and $(CH_3)_3NBF_3$ was detected when the tetrafluoroborate ion was used. None of the mixed fluoride/iodide complexes were observed. The acetate ions did not give rise to any new products; after heating the sample at 50°C for two days only $(CH_3)_3NBI_3$ could be detected.

Labelled triiodide adduct was used in two instances to see if boron exchange was occurring when this adduct reacted with tetrahaloborate ions. If boron exchange was found to occur, this would be strong support for a mechanism involving dissociation of the B-N bond. $Bu_4N^+BBr_4^-$ and $Et_4N^+BCl_4^-$ were the two salts chosen. In the former case, the presence of the butyl proton resonance precluded any definite conclusions from being drawn. After several days at 50°C the seven line multiplet of $(CH_3)_3N^{10}BBr_3$ could not be found. The boron-11 decoupler made no difference to the spectrum indicating that if exchange had occurred, then it was without breakage of the B-N bond. The results from the second mixture were

of much more interest and allowed important conclusions to be drawn. Heating the sample for two days produced a bump at about 180 Hz -- a hint of the trichloride complex. Further heating encouraged the reaction to continue. The concentration of this product increased, thus allowing positive identification of $(CH_3)_3N^{10}BCl_3$ (Figure 17). Halogen exchange was seen to be occurring without the B-N bond being broken.

F. SOME REACTIONS OF TRIMETHYLAMINE BORANE (TMAB)

Many reactions of TMAB have been well documented (156-159); among the more interesting -- as far as this work is concerned -- are the halogenation reactions of that complex. One or more borane protons have been replaced by halogen atoms using such reagents as hydrogen halides (155, 156), halogens (156), dimethylchloramine (172) and boron trihalides (171). Some of these reactions were repeated under slightly different conditions and some new experiments were devised in an effort to understand more about this type of reaction. In nearly all cases the reactions carried out were analogous to those used for the boron trihalide adducts.

The data listed in Table 18 consists of the chemical shifts of the methyl proton signals of the haloborane adducts. These signals are broadened slightly, by

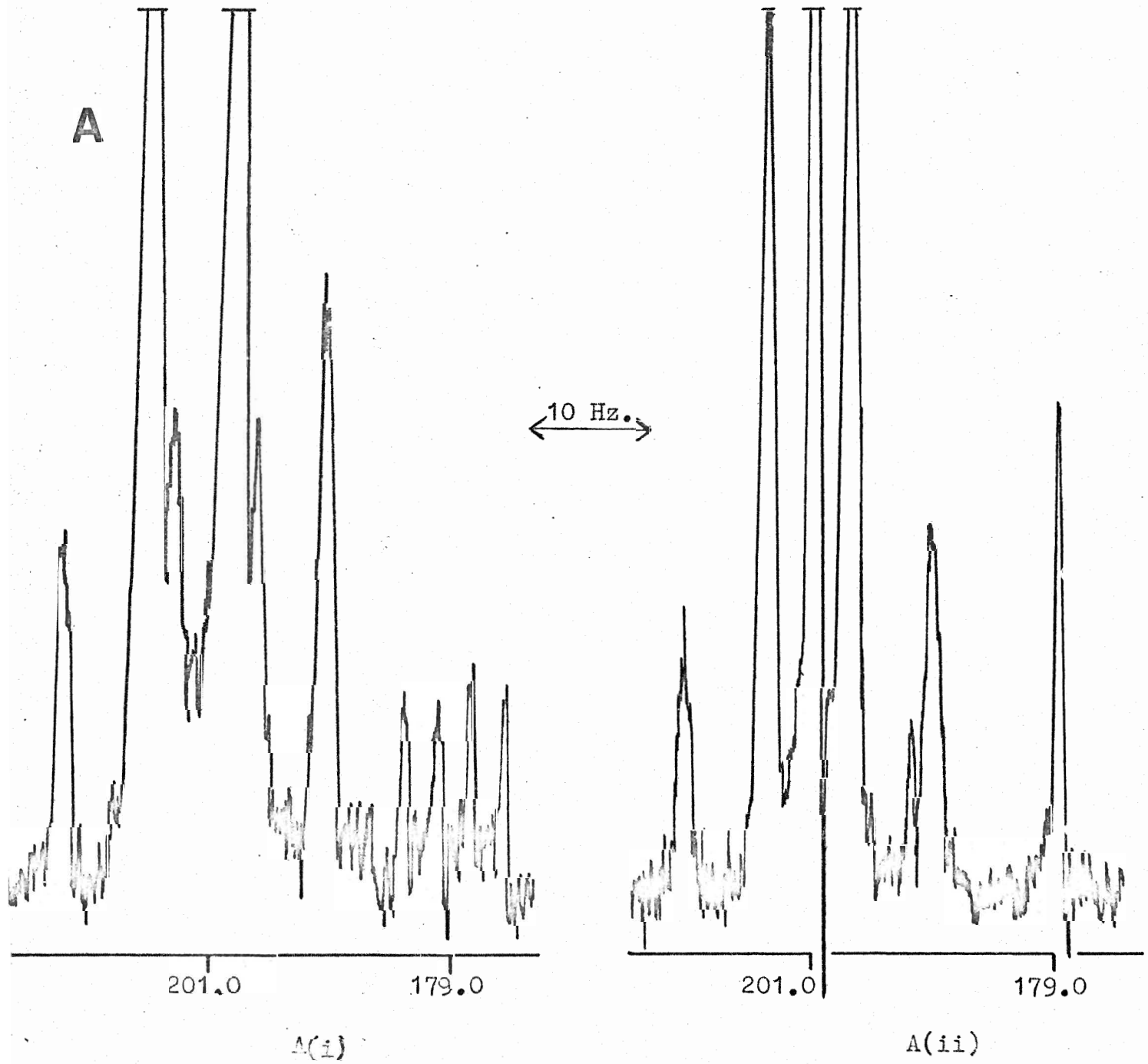
FIGURE 17

^{1}H N.M.R. Spectra of:-

A) $(CH_3)_3NBI_3 + Et_4N^+BCl_4^-$ i) Normal

ii) ^{11}B decoupled

B) $(CH_3)_3N^{10}BI_3 + Et_4N^+BCl_4^-$ (Normal)



A(i)

A(ii)

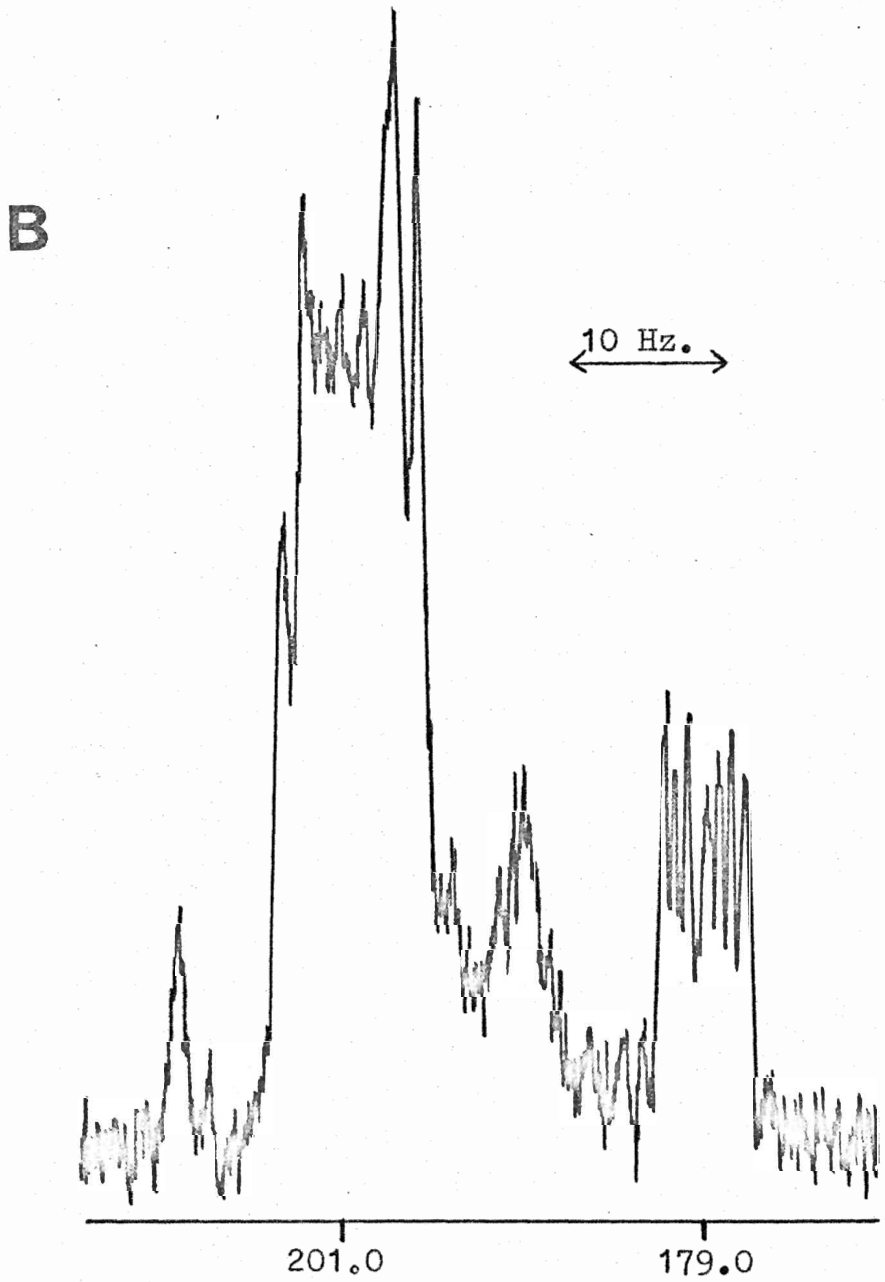

B
10 Hz.
201.0
179.0

TABLE 18 ^1H N.M.R. Data for Trimethylamine Haloborane Adducts*

Me_3N complexed with:	Methyl Protons ppm[a]	Hz[a]	$J^1H - {}^1H$ Hz
BH_3	2.61	156.6	0.5
BH_2Cl	2.64	158.4	0.3
$BHCl_2$	2.73	164.0	-
BH_2Br	2.72	163.2	0.3
$BHBr_2$	2.87	172.2	-
BH_2I	2.82	169.1	-
BHI_2	3.02	181.2	-
BHClBr	2.82	169.0	-
BHBrI	2.96	177.6	-
BH_2F [b]	2.42	145.2	
BHF_2 [b]	2.32	139.2	

a: downfield from TMS

b: reference 174

* the chemical shifts of the borane protons are not included because they were not recorded.

coupling to boron, but in each case the splitting is too small to be measured. That it is present is confirmed by the increase in peak intensity and sharpness on boron-11 decoupling. This further allowed detection and measurement of the splitting between the methyl and borane protons in TMAB, DBH_2Cl and DBH_2Br. The former case showed a poorly resolved quartet (Figure 18); the latter two were triplets. The borane protons could only be detected in samples of TMAB, and were identified as a widely spaced quartet centred at 1.60 p.p.m. with $J1_{H-}11_B$ = 101 Hz. It is interesting to note that when the decoupler was used to irradiate the borane proton resonances, the quartet collapsed, but no single peak developed in place of it.

Reactions of TMAB with Free Boron Trihalides

Solution reactions

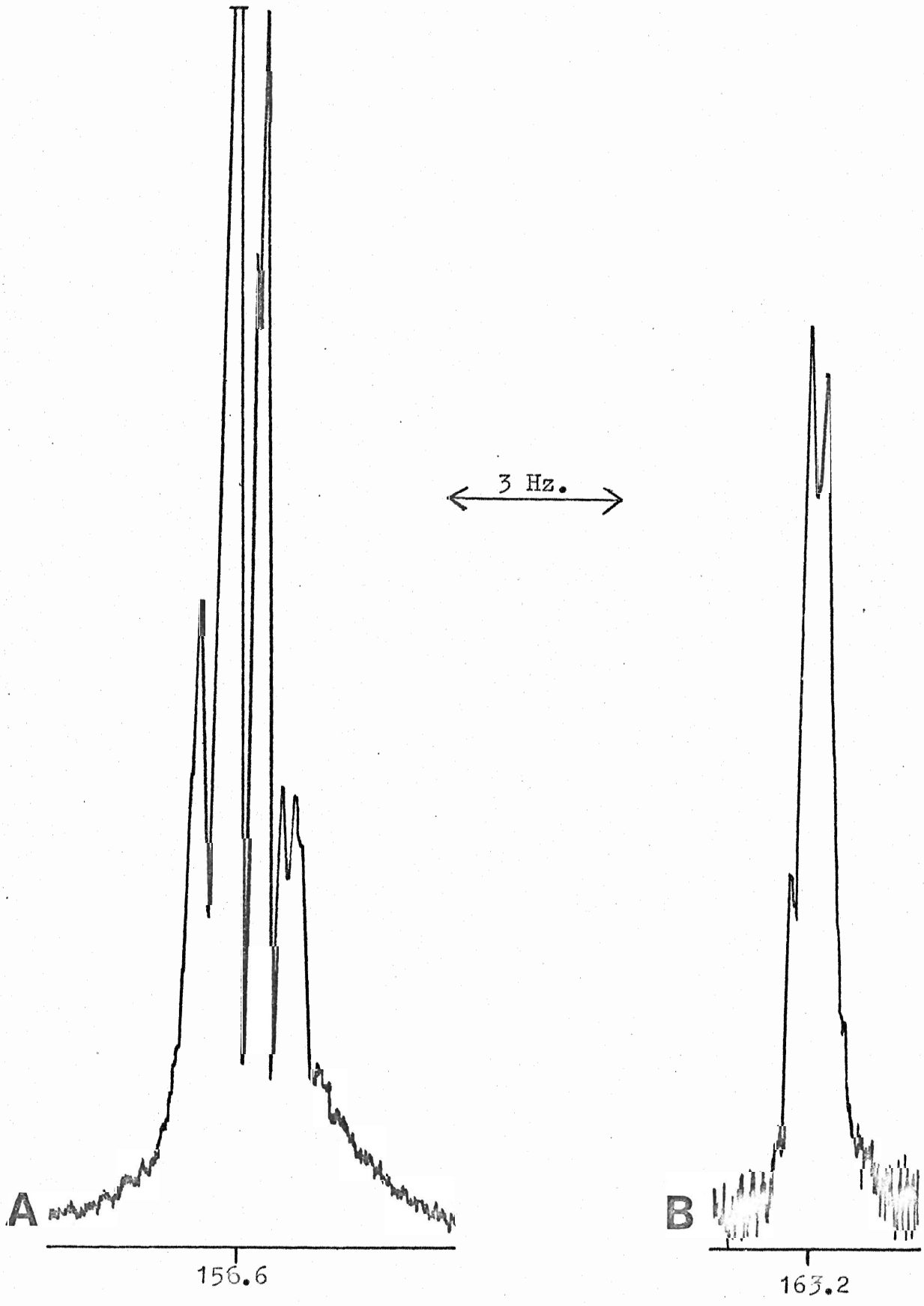
Boron trifluoride was bubbled through a solution of TMAB in methylene chloride and the resulting mixture analysed by N.M.R. The main difficulty with this system is that both TMAB and $(CH_3)_3NBF_3$ absorb practically in the same place and hence it is difficult, if not impossible, to tell when one or the other is present. However, if exchange did occur, then the borane proton quartet would be expected to diminish in intensity as the reaction proceeded and perhaps even disappear. Similarly the

FIGURE 18

^{1}H N.M.R. Spectra of:-

A) $(CH_3)_3NBH_3$ (^{11}B decoupled)

B) $(CH_3)_3NBH_2Br$ (^{11}B decoupled)


3 Hz.
A
156.6
B
163.2

production of mixed adducts would be recognizable because of their characteristic chemical shifts (174). During the the reaction the borane quartet remained -- even after heating for six hours -- and no mixed adducts were detected. It was thus apparent that boron trifluoride did not displace diborane; this is not surprising since BF_3 and BH_3 have similar acid strengths toward trimethylamine (28, 63).

With BCl_3 as the free acid, reaction occurred fairly rapidly at room temperature to form mixed adducts. Further reaction continued when the sample was heated, the concentration of the parent and mixed adducts diminishing as the trichloride adduct was formed.

Boron tribromide reacted very vigorously with a solution of TMAB and bubbles of a gas, probably diborane, were evolved. Analysis showed the presence of mixed adducts and a trace of $(CH_3)_3NBBr_3$. Further additions of the Lewis acid caused the concentration of the tribromide complex to increase.

Similar results were noted with boron triiodide. Diborane was evolved and all three adduct peaks were detected.

Gas phase reactions

TMAB was sealed separately into a combustion tube with each of the boron trihalides and heated for 3 hours at 120°C. In the first sample, that containing TMAB

and boron trifluoride the resulting N.M.R. spectrum showed only one resonance at 156.5 Hz. This was a rather broad envelope, that lacked the fine structure normally associated with $(CH_3)_3NBF_3$. The quartet seen on decoupling was of little diagnostic value since both the borane and trifluoride adducts give rise to this type of resonance. The widely spaced quartet of the borane protons was not detected; there is no satisfactory explanation for this at present. Thus the majority of N.M.R. evidence allows few conclusions to be drawn. It is probable that the broad resonance represents contributions from both $(CH_3)_3NBF_3$ and TMAB. Miller and Onyszchuk (157) showed that BH_3 was 80% displaced by BF_3 in a similar reaction at a higher temperature. The mixed adducts of this system were not detected either.

The other three samples were similar in that only two adducts were seen in each case -- namely, the mixed species. There was no trace of either parent adduct. The mixed adduct peaks could not be resolved into the expected doublet and triplet caused by coupling with the borane protons. Typical spectra are shown in Figure 19.

Reactions of TMAB with Trihalide Adducts

Mixtures of TMAB with a trihalide adduct -- in a 1 : 1 mole ratio -- were heated at 120°C for 3 hours. The spectrum from the system containing the trifluoride

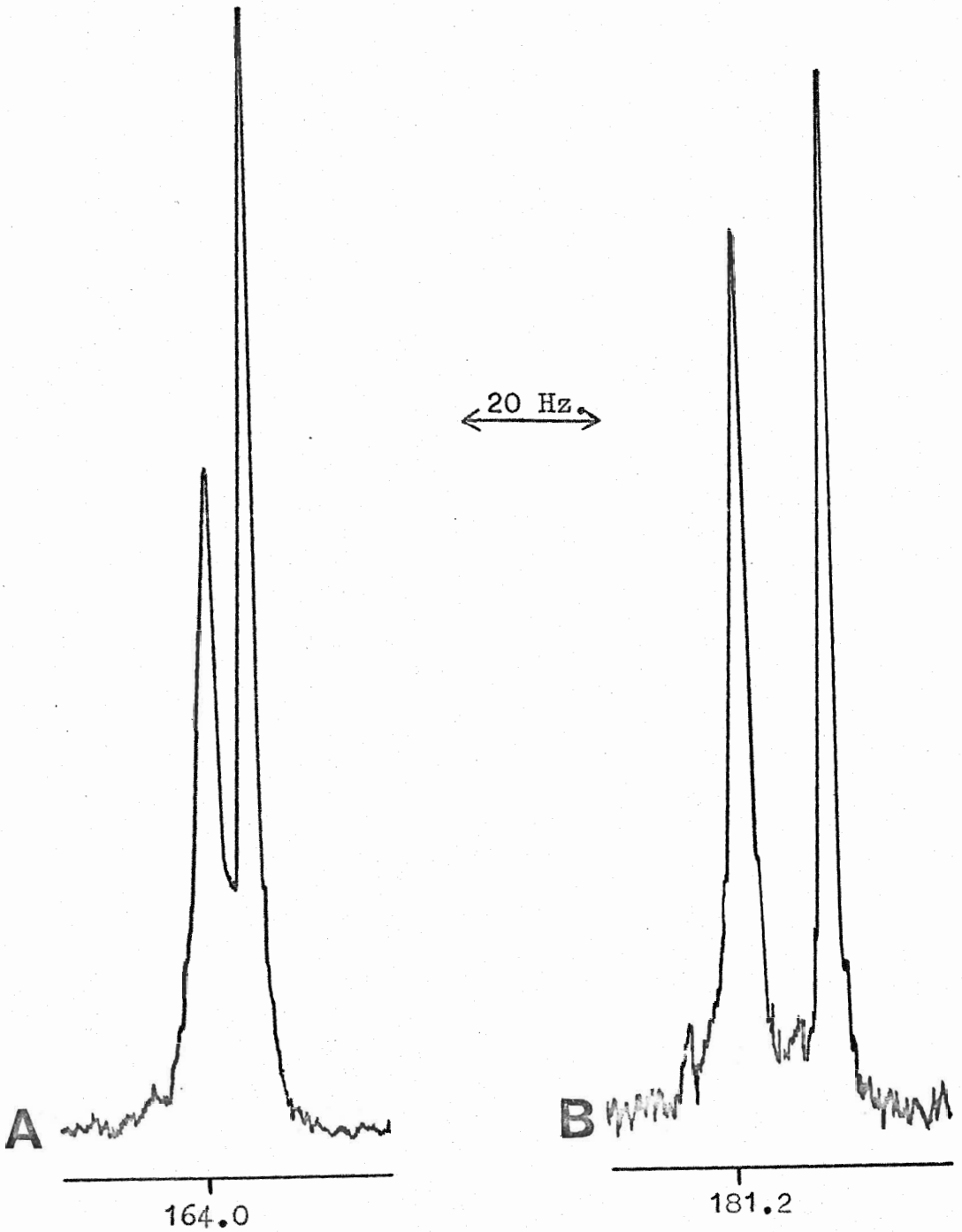
FIGURE 19

^{1}H N.M.R. Spectra of:-

A) $(CH_3)_3NBH_3$ + BCl_3

B) $(CH_3)_3NBH_3$ + BI_3

after being heated at 120°C for 3 hours.


20 Hz
A
164.0
B
181.2

complex showed a single broad resonance at 156 Hz. This was probably a composite envelope with contributions from both TMAB and $(CH_3)_3NBF_3$, although it was not possible to resolve either into separate entities, even when the heteronuclear decoupler was used. The borane proton quartet was detected and collapsed when irradiated; no alternative signal was seen when this happened.

When $(CH_3)_3NBCl_3$ and $(CH_3)_3NBBr_3$ were the trihalide complexes used, exchange reactions occurred only to a very limited extent. The appearance of peaks at 158 Hz and 164 Hz in the chlorine containing system, and at 164 Hz and 174 Hz in the third sample clearly indicated the presence of mixed haloborane adducts. However their concentrations were very low; $(CH_3)_3NBHBr_2$ could be seen only when the decoupler was used to increase peak intensity. Contrasting with this is the sample containing a mixture of the triiodide adduct and TMAB. After the reaction time had elapsed there was a notable absence of any violet colour which would have been an indication of decomposition. The N.M.R. spectrum showed that both TMAB and $(CH_3)_3NBI_3$ had completely disappeared. Two new broad singlets were present at 171 Hz and 184 Hz, these sharpening considerably on application of the decoupling frequency. They were assigned to $(CH_3)_3NBH_2I$ and $(CH_3)_3NBHI_2$ respectively. An unsuccessful attempt was made to record the borane proton quartets of these complexes.

Reactions of TMAB with Halogens

These reactions were undertaken in order to determine whether this would be a feasible route to prepare mixed adducts. Bromine and iodine were chosen as reactants because of their relative ease of handling and the reactions were carried out simply by mixing solutions of the halogens with solutions of TMAB. The course of the reaction was followed by N.M.R.

The addition of bromine solution caused the smooth evolution of a colourless gas -- probably hydrogen -- and the decolourisation of the halogen solution. The spectrum recorded immediately after this first addition contained one new broad singlet, which had a chemical shift that identified it as the monobromoborane complex. Further small increments of bromine increased the intensity of this resonance, and encouraged another to form at 173 Hz. The latter was assigned to the dibromoborane adduct. As the bromination continued the rate of reaction decreased; it was considerably more difficult to replace a second hydrogen atom with bromine, as indicated by the lingering yellow colour after halogen addition. The end result -- after a large excess of free bromine had been added -- was the formation of $(CH_3)_3NBBr_3$, clearly recognized by its characteristic chemical shift. The reaction proceeded in a stepwise fashion; $(CH_3)_3NBH_2Br$ was formed in large

quantities before the dibromoborane adduct was detected. Similarly very little $(CH_3)_3NBBr_3$ could be seen when $(CH_3)_3NBHBr_2$ was at a maximum concentration. Thus these mixed adducts could be prepared with only small amounts of contamination.

The reaction with iodine proceeded more slowly than the reaction with bromine; decolourisation occurred and a colourless gas was evolved. Analysis showed that $(CH_3)_3NBH_2I$ was formed. This agrees with the previously published work of Ryschkewitsch and co-workers (172). When the concentration of this adduct was at maximum -- no more TMAB was present -- further additions of iodine merely turned the solution purple. No further reaction resulted even when the mixture was refluxed at 50°C for several days. It was apparent therefore that iodine would not react with $(CH_3)_3NBH_2I$ to give the other mixed adduct and the triiodide complex.

A new adduct was prepared by using these reactions in turn. $(CH_3)_3NBH_2Br$ was prepared by the addition of a suitable quantity of bromine. This solution was then refluxed with iodine for 24 hours. A new peak appeared in the N.M.R. spectrum at 177 Hz indicating the formation of $(CH_3)_3NBHBrI$. The reaction did not proceed further. When bromine and chlorine were added separately to a small portion of this solution, iodine was, not surprisingly, displaced.

The isolation and characterisation of $(CH_3)_3NBHClBr$

This ternary borane adduct was prepared in two stages. $(CH_3)_3NBH_2Cl$ was prepared by bubbling excess hydrogen chloride through a solution of TMAB. The monochloroborane complex was then allowed to react with bromine, the reaction being quenched when the N.M.R. spectrum indicated that only the desired product was present. This compound has been detected previously (240) although details of its preparation were not published at that time. The methyl protons of the complex absorbed as a broadened singlet at 169 Hz; fine structure -- both coupling to boron, which was previously reported to be non-existent (240) and the borane proton -- could not be resolved. No resonance for the latter proton could be detected. The I.R. spectrum of this compound is shown in Figure 20 and the mass spectrum is listed in Table 19. Most ions were assigned after consideration of the isotopic patterns displayed. Where no initial fit between theoretical and observed intensities was possible, an effort was made to calculate the contribution of different ion combinations to the measured intensity. The best results are listed in Table 19. Some interesting points can be drawn from the table. No molecular ion can be seen; this is not surprising since the Lewis acid strength of the substituted borane, as estimated from N.M.R. evidence, falls below that

FIGURE 20

The I.R. Spectrum of $(CH_3)_3NBHClBr$

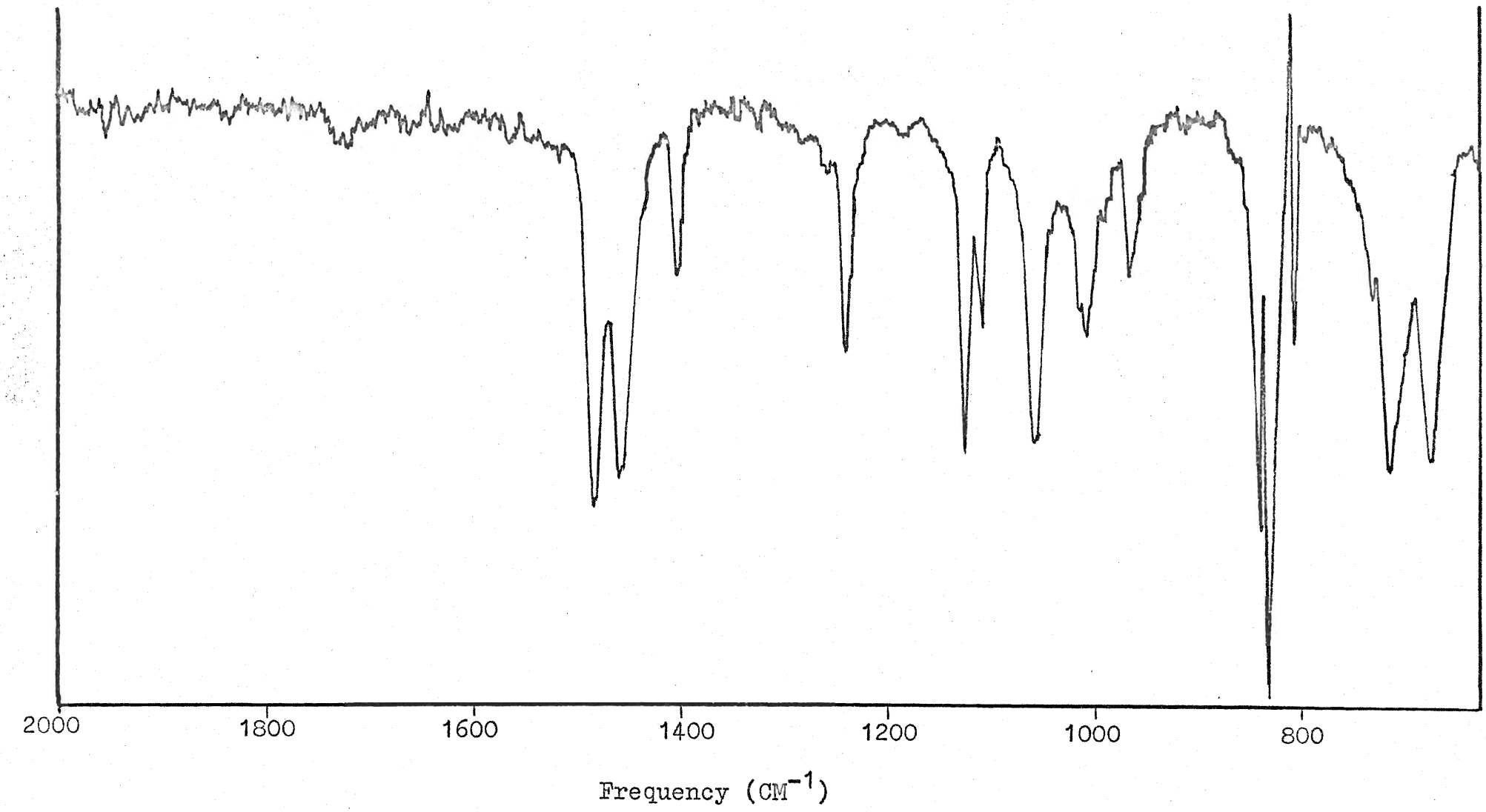

2000
1800
1600
1400
1200
1000
800
Frequency (CM^{-1})

TABLE 19 The Mass Spectrum of $(CH_3)_3NBHClBr$

m/e	Intensity	% total ion current (a)	Proposed structure
232	0.58		
231	0.30		$(CH_3)_3NBBr_2^+$: formed by rearrangement of parent to give $(CH_3)_3NBClBr_2$, followed by loss of Cl•
230	1.5	0.58	
229	0.49		
228	0.96		
227	0.23		
210	0.34		
209	0.093		
208	1.7		$BClBr_2^{+\bullet}$: formed by rearrangement of parent, as above, and loss of $(CH_3)_3N$.
207	0.47	1.03	
206	2.6		
205	0.70		
204	1.1		
203	0.27		
189	0.093		
188	0.069		
187	4.1		$(CH_3)_3NBClBr^+$: formed either by loss of H• from parent, or by rearrangement.
186	16.0	6.94	
185	5.8		
184	20.3		
183	2.3		
182	5.2		
181	0.19		

m/e	Intensity	% total ion current	Proposed structure
174	0.56		
173	2.3		
172	1.5		
171	2.9	2.12	51.1% BBr_2^+
170	2.9		and
169	2.3		48.9% $C_2H_5NBClBr^+$
168	1.5		
167	0.99		
164	0.27		
163	0.70		
162	0.65	0.34	$BCl_2Br^{+\cdot}$
161	0.19		
160	0.49		
159	0.12		
153	0.42		
152	10.2		
151	3.2		
150	11.6	4.13	$C_3H_{10}NBBr^+$
149	3.2		
148	0.26		
147	0.23		

m/e	Intensity	% total ion current	Proposed structure
144	0.23		
143	0.12		
142	1.5	0.70	$(CH_3)_2NBCl_2^+$
141	0.47		
140	2.03		
139	0.58		
137	0.34		
136	5.8		
135	2.03	2.31	$C_2H_6NBBr^+$
134	6.4		
133	1.7		
131	0.12		
130	6.4		62.4% BClBr
129	8.7		and
128	16.6	15.85	
127	30.2		
126	19.8		37.6% BHClBr
125	23.3		
124	6.4		
123	0.12		

m/e	Intensity	% total ion current	Proposed structure
120	0.70		
119	0.23		
118	0.73	0.33	$3Cl_3^{+\cdot}$
117	0.26		
116	0.42		
109	1.4		
108	32.6		$(CH_3)_3NBHCl^+$; there is a possible small contribution (2.0%) from $BBrNH^+$
107	13.9		
106	100.0	24.83	
105	25.6		
104	0.93		
103	0.41		
94	0.69		
93	8.1		
92	11.9	9.79	$(CH_3)_2NBCl^+$
91	8.1		
90	30.2		
89	9.0		
88	0.69		
87	0.23		

m/e	Intensity	% total ion current	Proposed structure
83	11.9		
82	25.6		Br^+ and HBr^+
81	18.9	13.86	
80	27.9		
79	13.3		
63	2.6		
62	1.4		
61	9.6	17.17	$(CH_3)_3N^{+\cdot}$ and $C_3H_8N^+$
60	2.9		
59	44.2		
58	41.9		
57	12.5		
56	5.8		

(a) All figures represent the sum of polyisotopic contributions.

of $BFBr_2$, the only other mixed adduct known to give a parent ion. Similarly, the abundance of $C_3H_9N^{+\cdot}$ and $C_3H_8N^+$ indicated that the strength of the B-N bond is intermediate between that of $(CH_3)_3NBFBr_2$ and $(CH_3)_3NBClBr_2$.

The most abundant ion is $(CH_3)_3NBHCl^+$, formed by loss of bromine from the parent. This is expected since heavier halogen atoms are normally more easily removed (70).

The Reaction of TMAB with some Hydrogen Halides

The samples used for these studies consisted of three different preparations of HX (X = Cl, Br and I) with TMAB. These consisted of a TMAB : HX ratio of 1 : 1, 1 : 10 and 1 : 1 with a trace of water. The only product detected in those samples containing equimolar quantities of both reactants was trimethylamine monohaloborane. This was formed as expected (155, 156) immediately on warming the tube to ambient temperatures. The sample to which a trace of water had been added still contained a small quantity of TMAB when first inspected, but this disappeared when the tubes were heated. This may indicate that a slower ionic reaction mechanism is operative.

Further reaction was seen to occur when the hydrogen halide was present in a large excess. After heating the sample for several days at 50°C, trace amounts of the dihaloborane adducts showed up in the spectrum. This

low concentration was expected since halogenation is known (173) to progressively deactivate remaining B-H bonds toward further reaction.

The Reaction of TMAB with some Ionic Species

Previous experiments have shown that halogen exchange does not occur when ionic halides are mixed with the boron trihalide adducts of trimethylamine, excepting the triiodide complex. It seemed of interest therefore to investigate the analogous reactions of TMAB. Using chloroform as a solvent, samples containing the adduct with $Et_4^+NCl^-$ or $Et_4^+NBCl_4^-$ were prepared. The reactions were also carried out using excess free Lewis base. No exchange reaction occurred, even after heating for several hours at 90°C. Some decomposition was evident in the sample containing BCl_4^- and free trimethylamine; a small amount of $(CH_3)_3NBCl_3$ formed over the period of several days.

The Reaction of TMAB with Phosphorus Pentachloride

Small portions of phosphorus pentachloride were added to a solution of TMAB in methylene chloride. The N.M.R. spectrum was recorded after each addition. The first analysis showed a broad resonance at about 157 Hz. Decoupling suggested the peak was a doublet, but a closer

inspection proved that the signal was a singlet at 158 Hz and a quartet at 156 Hz. These were assigned to $(CH_3)_3NBH_2Cl$ and TMAB respectively. The quartet was caused by coupling of the methyl protons with the borane protons. Further additions of PCl_5 caused $(CH_3)_3NBH_2Cl$ to increase in concentration at the expense of TMAB, and later caused the appearance of $(CH_3)_3NBHCl_2$. Continued increments of phosphorus pentachloride changed the relative peak sizes and led to the development of a quartet centred at 179 Hz. This was easily identified as $(CH_3)_3NBCl_3$. Time was spent on trying to obtain a triplet and doublet on the boron-11 decoupled spectra of the chloroborane adducts. Results were not generally reproducible and it was assumed that the coupling constant is at or just above the limit of resolution.

CHAPTER IV

DISCUSSION

A. LEWIS ACIDITY BY N.M.R. MEASUREMENTS

The results of an investigation (267) into the triethyl derivatives of aluminium and gallium and their diethyl etherates revealed that the apparent electronegativity of the Group III acceptor atom is diminished on complex formation and the electronegativity of the donor atom is increased. On the basis of these results, Coyle and Stone (257) suggested that the internal chemical shift -- the difference between methyl and methylene proton resonances in ethyl groups -- might be useful in predicting the relative stabilities of some donor-acceptor complexes. Accordingly, they measured the internal shifts of a series of molecular addition compounds for which the stabilities were known. Their results were not uniformly encouraging. Thus, internal shifts showed the acceptor power of some boranes toward triethylamine to decrease in the order $BF_3 > BH_3 > BMe_3$; calorimetric evidence suggested the order to be $BF_3 \backsimeq BH_3 > BMe_3$. The internal shift-adduct

stability correlation was also found to be inapplicable to the ethyldimethylamine adduct system. However, the chemical shift sequence of a series of trimethylamine adducts indicated the order of acidity to be $BF_3 \eqsim BH_3 > BF_2Et \eqsim BF_2Vi > BMe_3$; an order in agreement with other data (257).

Other research has also shown N.M.R. to be a useful tool in assessing donor-acceptor interaction. The relative base strengths of some substituted aminophosphines toward triethylborane, estimated from proton N.M.R. measurements (268), were found to be in the same order as that predicted by displacement reactions, namely $(CH_3)_3P > (CH_3)_3N \eqsim (CH_3)_2PN(CH_3)_2 > CH_3P[N(CH_3)_2]_2 > P[N(CH_3)_2]_3$. The relative base strengths of some ethers have been estimated from the proton and fluorine chemical shifts of their BF_3 adducts (87). It has been suggested (269) that ^{11}B chemical shifts may be regarded as empirical constants which may be used for identification purposes; other workers investigated the boron-11 chemical shifts of some ketone and tertiary amine adducts and concluded that the data allowed direct comparison of the acceptor strength of the boron trihalides (270).

Miller and Onyszchuk (188) have shown the existence of a linear relationship between the methyl proton chemical shifts of trimethylamine BX_3 complexes (X = H, F, Cl, Br)

and their heats of formation and dipole moments. This may be taken as satisfactory evidence to indicate that for the trimethylamine-boron trihalide system, N.M.R. data can be correlated to Lewis acid strength.

B. ACCEPTOR POWER OF THE BORON TRIHALIDES

Using proton complexation shifts as a suitable yardstick, we find that the acceptor power of the boron trihalides (both simple, mixed, and some haloboranes), toward trimethylamine, decreased in the order:

$BI_3 > BBrI_2 > BBr_2I > BClI_2 > BBr_3 > BClBrI > BClBr_2 > BCl_2I > BCl_2Br > BFI_2 \simeq BHI_2 > BCl_3 > BFBrI > BHBrI > BFBr_2 > BFClI > BFClBr > BHBr_2 > BFCl_2 > BH_2I \simeq BHClBr > BF_2I > BF_2Br > BHCl_2 > BH_2Br > BF_2Cl > BH_2Cl > BF_3 \simeq BH_3 > BH_2F > BHF_2$.

The above order may be rationalized in the following manner. As the acceptor power of the acid increases, the electron pair in the B-N bond will progressively become more tightly bound to boron. Electron release from the methyl groups will compensate for this decrease in electron density on nitrogen. The resultant deshielding of the CH_3 groups causes their proton resonances to shift to lower field. However, as has been pointed out before (188), this explanation may not be the only one.

Since the mixed boron trihalide adducts have

chemical shifts intermediate between those of the unmixed adducts, the Lewis acidity may be related to a simple additivity of different halogens. Thus BH_2I and BHClBr have the same apparent Lewis acidity; BFClI and $BFBr_2$, too, have similar acceptor power. It is worth noting that BFI_2 and BHI_2 have almost identical acidities. The same can be said of their parents, BF_3 and BH_3. However, it is interesting that BH_2I and BF_2I present an anomaly; the former is a stronger acid than the latter. The significance of this is not clear at present. The behavior of BH_3 as a Lewis acid is obviously somewhat different from the boron trihalides, and the same is probably true for the haloboranes. The fact that BH_2I and BHI_2 adducts are far more stable than BF_2I and BFI_2 complexes -- as determined from gas phase reactions -- indicates that hydrogen and iodine exist together on boron more readily than fluorine and iodine. This may have some bearing on the relative Lewis acidities. The chemical shift values of the BH_2F and BHF_2 adducts included in Table 18 are those of Van Paaschen and Geanangel (174). It seems unusual that the methyl proton resonances shift progressively to high field as two fluorine atoms successively replace hydrogen in BH_3. These results then, are anomalous; they may either refute N.M.R. evidence as a basis for judging Lewis acidity or the chemical shifts do not correspond to the

proposed molecular addition compounds. Other evidence concerning fluoroborane adducts may be drawn from the results of the gas phase reactions between TMAB and BF_3 or $(CH_3)_3NBF_3$. Mixed adducts were not detected in either case although it has previously been shown that BF_3 will displace BH_3 from TMAB (157). Such conditions should be favourable for the production of mixed fluoroborane adducts especially if other $(CH_3)_3NBH_3/BX_3$ systems can be taken as typical reactions. It is of particular interest that BF_2I and BFI_2 have been included in the above order of Lewis acidity. These mixed boron trihalides could not be detected by N.M.R. as uncomplexed molecules (212, 248), although their positive ions have been identified by mass spectrometry (218). Complexation with trimethylamine stabilised these species just sufficiently to enable their detection, although the concentration of each was low. A study of this system carried out by adding different concentrations of BI_3 to a solution of $(CH_3)_3NBF_3$ revealed that the mixed adducts were formed in an approximately constant, but low concentration. Additional reaction time did not increase the proportion of them, and a higher concentration of BI_3 merely resulted in the reaction going more towards completion. Thus an unfavourable equilibrium is responsible for their relative instability, suggesting that fluorine and iodine do not readily coexist on boron.

Steric interactions may destroy a greater amount of the π-bonding between the boron and fluorine causing the latter to be less tightly bound.

Anomalous reactions have also been noted in the dimethyl ether BF_3/BI_3 system (238) and in studies of phosphine/mixed boron trihalide adducts (110). It seems possible in the former case that an excess of BI_3 would react with mixed F/I adducts to give ionic species such as $(CH_3)_2OBI_2^+BF_4^-$. (238).

The downfield shift of the adduct methyl proton resonance is paralleled by a regular increase in the $^1H - ^{11}B$ coupling constant as heavier halogens replace lighter halogens. It is tempting therefore to relate the magnitude of the interaction to the strength of the donor-acceptor bond and possibly predict acceptor strength. Rudolph and Schultz (271) have shown such a relationship exists between the size of the $^{11}B-^{31}P$ coupling constant and the dative bond strength in a series of substituted phosphine BX_3 complexes, (X = H, F, Cl, Br). Another similar study (129) augmented these findings. However the empirical correlation was found to be invalid (271) when Me_3P was complexed with BX_3 (X = H, F, Cl, Br).

Spin-spin coupling in amine adduct systems is probably dominated by the Fermi contact term and therefore it should be possible to relate the coupling constant to

the S character which each atom contributes to the coordinate bond. This has been done successfully for a series of mixed boron trihalide phosphine adducts (110).

The regular increase in the ^{1}H-^{11}B coupling constant may be explained because the coupling must be transmitted across the dative bond. As the electron density in the B-N bond increases -- it does so as the Lewis acidity of the boron trihalides becomes greater -- the coupling constant also increases.

The poorly resolved 1 : 1 : 1 : 1 quartets due to ^{11}B coupling which we observed in the ^{1}H spectra of $(CH_3)_3NBF_3$, other fluorine containing adducts and the haloborane complexes are probably the result of partial quadrupole relaxation of boron (265). Nuclei with spin greater than I =1/2 have quadrupole moments which couple strongly to local electrical fields by means of molecular reorientations. Electric fields arise from the asymmetric distribution of nuclear charges. The greater the nuclear asymmetry, the stronger is the electric field gradient and the more effective is the quadrupole relaxation. The nucleus with $I > 1/2$ is seen in an average of its spin states and observation of the separate spin-couplings is more difficult. The expected spin multiplet may be resolved only when the nuclei with $I > 1/2$ have a small quadrupole moment or are in a highly symmetrical environment. The

nuclear quadrupole moment of boron-11 is sufficiently small to enable ^{1}H-^{11}B coupling to be observed in many boron trihalide addition compounds. Fields external to the molecule are apparently unimportant since in the spectra of salts of boron cations, namely two tertiary amines co-ordinated to a BH_2^+ group, well defined multiplets are observed (159).

Little information can be deduced for the BF_2X and BFX_2 adducts because residual ^{1}H-^{19}F coupling tends to complicate the resonance. It would be interesting to spin decouple the fluorine in an attempt to measure $J^{1}_{H-^{11}B}$ for these adducts.

$(CH_3)_3NBCl_3$ gives a sharper and more well defined quartet than the BBr_3 and BI_3 adducts. This better definition is more apparent in the ^{1}H spectra of the boron-10 labelled adducts. The spectrum of $(CH_3)_3N^{10}BCl_3$ is an even septet. Those of the tribromide and triiodide complexes show definite collapse; this can be partially reduced to yield better septets by heating the sample to 70°C, a further confirmation of the assignment to quadrupole broadening. Thus $(CH_3)_3NBCl_3$ apparently has a higher symmetry than $(CH_3)_3NBBr_3$ and $(CH_3)_3NBI_3$. The relative size of the halogen atoms undoubtedly makes an important contribution to this property; chlorine atoms are closest in size to methyl groups.

The value $J1_{H-}{}^{10}{}_{B}$ = 0.9 Hz, measured for $(CH_3)_3N^{10}BCl_3$ agrees well with the value of Ryschkewitsch and Rademaker (240). Thus the value of the ratio $J10_B : J11_B$ = 0.32 also agrees with the value of 0.35 calculated from the gyromagnetic ratios of boron-10 and boron-11. However, Ryschkewitsch and Rademaker (240) suggested that proton-boron coupling was destroyed when hydrogen or fluorine was a substituent on boron. This lack of coupling was attributed to efficient quadrupole relaxation when the field gradient was increased by substitution. This of course is erroneous since all trimethylamine adduct resonances -- whether quartets or broadened single peaks -- collapse to a single sharp line when decoupled with the appropriate boron-11 frequency. As suggested above, the broad peaks observed for fluoroboron halide and haloborane adducts are the result of three factors; namely a small value $J1_{H-}{}^{11}{}_{B}$, partial quadrupole collapse and residual $^{11}B-^{19}F$ or $^{1}H-^{1}H$ coupling. Thus the methyl peak of $(CH_3)_3NBF_3$ is a 1 : 3 : 4 : 4 : 4 : 4 : 4 : 4 : 3 : 1 decet (28). It is of interest that the long range $^{1}H-^{19}F$ coupling noticed in the fluorine containing adducts, and the similar $^{1}H-^{1}H$ coupling in the haloborane complexes shows little dependence on the Lewis acid strength of the acceptor. This contrasts with the regular methyl proton-boron-11 coupling.

^{19}F N.M.R. Parameters

Table 20 shows a comparison of the fluorine-19 chemical shifts and coupling constants of the fluorine containing boron trihalides and their trimethylamine adducts. Each free trihalide showed as a 1 : 1 : 1 : 1 quartet caused by coupling to boron-11. The same was true of the adducts unless they contained boron-10 when a 1 : 1 : 1 : 1 : 1 : 1 : 1 septet was recorded.

Complexation with trimethylamine allowed measurement of the chemical shifts and coupling constants of BF_2I and BFBrI, both of which were not detected as simple mixed trihalides. BFI_2 and BFClI were also known to be present -- they had been identified by proton N.M.R. -- in similar systems. Their low concentration apparently precluded their detection.

Generally there is a downfield shift and a gradual increase in the coupling constant as heavier halogens are substituted for the lighter fluorine atoms. A similar pattern has been observed for the free trihalides (224), their dimethyl ether complexes (238), the 4-methylpyridine adducts (244) and the tetrahaloborate ions (236). In the free boron trihalides there is a near linear relationship between the ^{19}F chemical shifts and $J11_{B-}{}^{19}{}_{F}$, provided the sign of the coupling constant in boron trifluoride is

TABLE 20 Comparison of ^{19}F N.M.R. Data of Free Boron Trihalides and their Trimethylamine Adducts

BX_3	FREE		COMPLEXED	
	^{19}F p.p.m.[a,b]	$J^{11}B-^{19}C$ Hz[c]	^{19}F p.p.m.[d]	$J^{11}B-^{19}F$[d]
BF_3		14.5	164.1	15.1
BF_2Cl	-51.5	33	143.3	44.8
BF_2Br	-68.4	58	134.0	54.2
$BFCl_2$	-99.0	73	132.6	69.5
BFClBr	-114.8	95	126.0	78.0
BFClI		102	*	*
$BFBr_2$	-130.4	121	120.8	89.3
BF_2I	-	-	119.6	65.8
BFBrI	-	189	112.7	100.0
BFI_2	-	-	*	*

---

a. p.p.m. downfield from BF_3

b. Reference 224.

c. Reference 112.

d. This work: p.p.m. upfield from $CFCl_3$

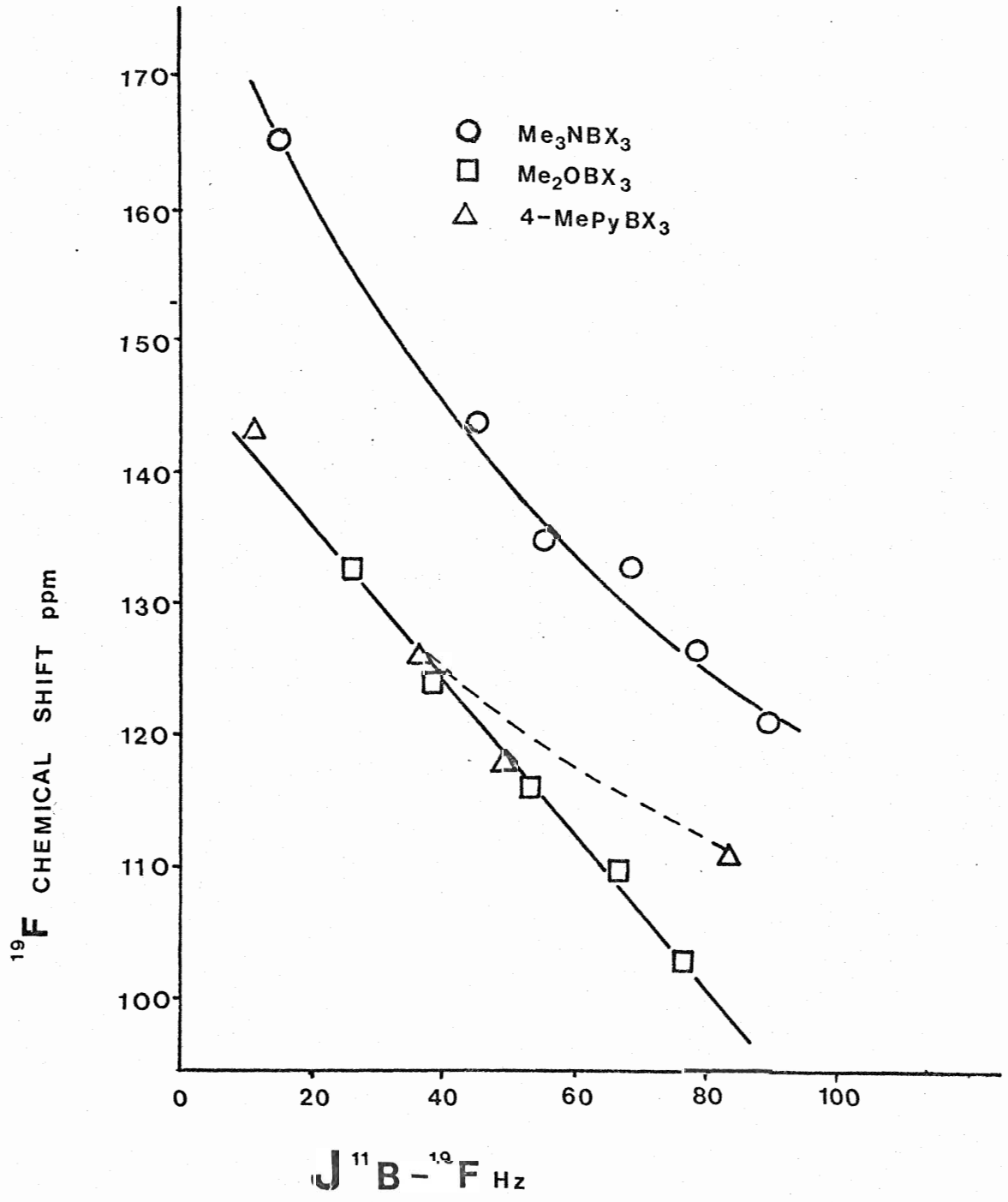
* too dilute to observe

assumed to be the opposite of that found in the other boron trihalides (238, 272). A similar near linear relationship exists for the Me_2O adducts. Figure 21 compares these plots and shows a small but significant deviation from linearity in the Me_3N complex series. The lack of such a relationship for the 4-methylpyridine series is also seen in Figure 21.

The ^{19}F chemical shift and coupling constant values of the free boron trihalides may be rationalized as follows. Theoretical work (225) and experimental data (226) have shown that ^{19}F shifts can be correlated with electron density on the fluorine atom; that electron withdrawal from the fluorine atom in BF_3 occurs with substitution of another halogen or organic group (273). This is contrary to expectations if electronegativity is considered a dominant factor. On the basis of an inductive effect the ^{19}F chemical shifts of BF_2X and BFX_2 would be expected to appear at higher fields than BF_3. Yet the opposite occurs. The normal explanation is that the amount of π back-bonding between fluorine and boron increases when substitution occurs (224). This results in progressive deshielding of the remaining fluorine atoms, with a corresponding increase in electron density in the B-F bond. For this work however, the factors which predominate in the chemical shift changes need not necessarily be those which

FIGURE 21

$\delta\ ^{19}F$ vs $J11_{B-}{}^{19}F$ for the Mixed Boron Trihalide Adducts.


170
160
150
140
130
120
110
100
0
20
40
60
80
100
^{19}F CHEMICAL SHIFT ppm
$J\,^{11}B-^{19}F$ Hz
Me_3NBX_3
Me_2OBX_3
4-MePyBX_3

predominate in the coupling constant changes. This may be particularly true for $(CH_3)_3NBF_2I$. The smaller changes in ^{19}F chemical shifts and coupling constants of adducts -- compared to free trihalides -- may indicate that π-bonding is not as important in the adducts as it is in the planar boron halides, not unexpected in view of the tetrahedral geometry of the adducts.

C. THE MECHANISM OF HALOGEN EXCHANGE

Possible mechanisms of substituent redistribution in three-coordinate and four-coordinate boron have been discussed by Lockhart (201). Exchange may occur in three-coordinate compounds via a bridged four-coordinate transition state B_2X_6. Such a mechanism has been proposed for the free boron trihalides (201, 49), the exchange being sufficiently rapid to prevent isolation of the mixed species but slow enough on the N.M.R. time scale to enable their detection. Four-coordinate compounds such as BX_4^- probably require a preliminary dissociation as a first step.

$$BX_4^- \longrightarrow BX_3 + X^- \qquad 1.$$

Exchange may then occur by either of the following routes:-

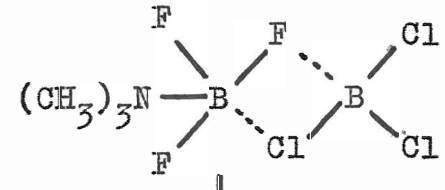
i) recombination with Y^-

$$BX_3 + Y^- \longrightarrow BX_3Y^- \qquad 2.$$

ii) reaction of BY_4^-, possibly via a halogen bridged intermediate similar to $B_2F_7^-$ (274, 275) and $Al_2X_7^-$ (276).

In the trimethylamine adduct system, an initial examination reveals there are two basic mechanisms worthy of consideration. The first involves only halogen exchange without rupture of the B-N bond. This reaction may proceed through a halogen bridged intermediate:-

$$(CH_3)_3NBF_3 + BCl_3 \longrightarrow$$



(See Fig.22)

$$(CH_3)_3NBF_2Cl + BFCl_2 \qquad 3.$$

Such a scheme has been proposed earlier (84) to explain fluorine scrambling among BF_3 complexes.

Alternatively it may involve an initial pre-ionization step (241) in which a halide ion is lost:-

$$(CH_3)_3NBF_3 \longrightarrow [(CH_3)_3NBF_2]^+ + F^- \qquad 4.$$

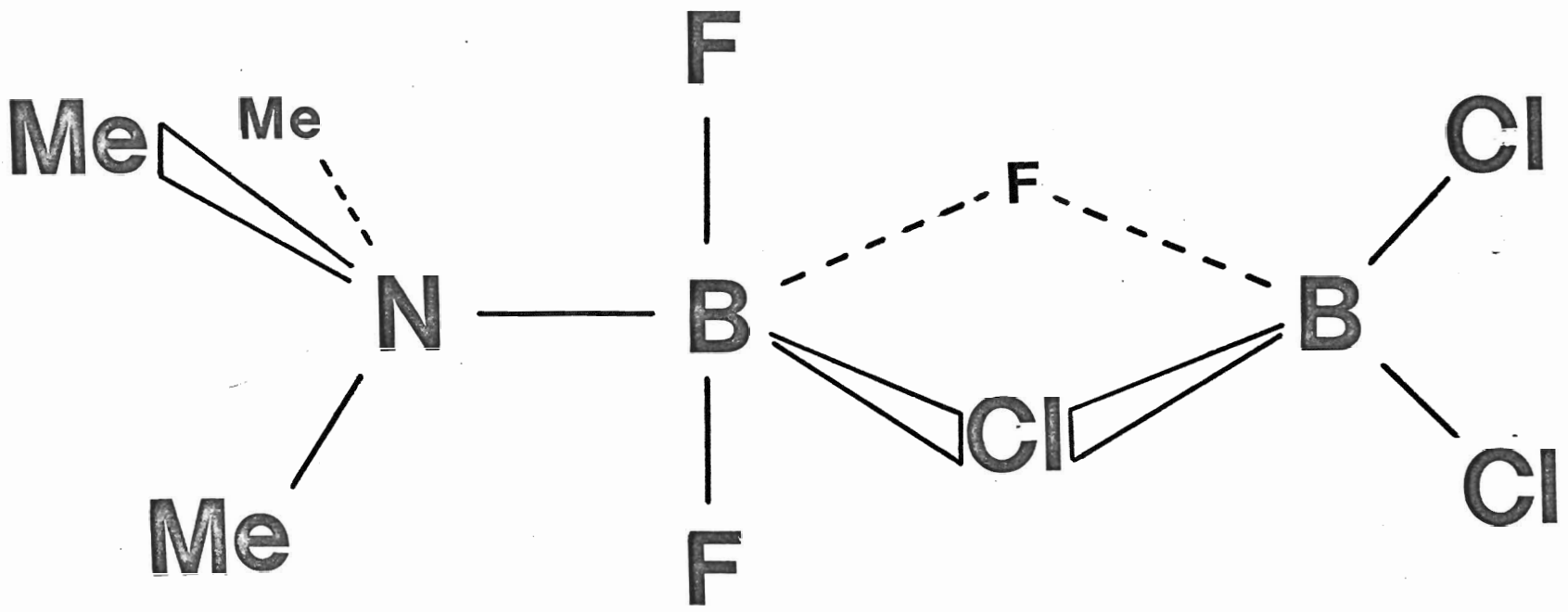
Further reaction could proceed via:-

$$[(CH_3)_3NBF_2]^+ + BCl_3 \longrightarrow (CH_3)_3NBF_2Cl + [BCl_2]^+ \qquad 5.$$

FIGURE 22

Diagrammatic Representation of the

Halogen Bridged Intermediate


F
Me
Me
Cl
F
N
B
B
Cl
Cl
Me
F

$$[BCl_2]^+ + F^- \longrightarrow BCl_2F \qquad 6.$$

$$\text{or } F^- + BCl_3 \longrightarrow BCl_3F^- \qquad 7.$$

$$\text{and } BCl_3F^- + [(CH_3)_3NBF_2]^+ \longrightarrow (CH_3)_3NBF_2Cl + BFCl_2 \qquad 8.$$

The second basic mechanism would involve breaking the B-N bond, followed by halogen scrambling among the free boron trihalides and recombination with the base.

$$(CH_3)_3NBF_3 \longrightarrow (CH_3)_3N + BF_3 \qquad 9.$$

$$BF_3 + BCl_3 \longrightarrow \begin{matrix} F & & F & & Cl \\ & \diagdown & & \diagup & \\ & & B & & B \\ & \diagup & & \diagdown & \\ F & & & & Cl \end{matrix}$$

$$\longrightarrow BF_2Cl + BFCl_2 \qquad 10.$$

$$BF_2Cl + (CH_3)_3N \longrightarrow (CH_3)_3NBF_2Cl \qquad 11.$$

It is evident from the results that adducts react rapidly in solution with free boron trihalides, particularly when the free acceptor is a stronger Lewis acid than that complexed. Use of boron-10 labelled adducts provided a convenient means for obtaining useful information about the behavior of the dative bonds during such reactions. The growth of seven-line resonances corresponding to $(CH_3)_3N^{10}BX_3$ (X = Cl, Br, I) during the

appropriate reactions is consistent with halogen exchange occurring without the donor-acceptor bond being broken. If such breakage was occurring it would be reasonable to expect the products to contain both boron isotopes in a ratio dependent on their relative initial concentrations. The small amount of ^{11}B observed when ^{11}B is noise decoupled is consistent with the 4% isotopic contamination of the starting material. Similar conclusions were drawn when an adduct was reacted with a weaker boron trihalide. The reactions were generally slower but nonetheless indicated that halogen scrambling occurred without exchange of boron; therefore without rupture of the B-N bond.

The exchange can probably be explained by one of the two basic mechanisms suggested above. Krishnamurthy and Lappert (241) have advanced a pre-ionization procedure to explain the reaction of $(CH_3)_3NBBr_3$ with BF_3 in methylene chloride. They found that when the concentration of each reactant was 0.2M, mixed adducts and $(CH_3)_3NBF_3$ formed after several days. Their argument was that pre-ionization:-

$$(CH_3)_3NBBr_3 \longrightarrow \left[(CH_3)_3NBBr_2\right]^+ + Br^- \qquad 12.$$

is to be expected in this system in which the ligand-boron bond is strong while the boron-halogen bond may be relatively easily heterolysed. Heaton and Riley (196) proposed a similar mechanism to explain the kinetics of solvolysis

of amine-boron trihalide complexes. However, it was also suggested (241) that the BF_3 and BCl_3 trimethylamine adducts would only undergo halogen exchange if a stronger Lewis acid was present. This work could not duplicate these results; only traces of mixed BF_3/BBr_3 adducts could be detected after several weeks when initial concentrations were 0.2M in each component. Reproducible results were, however, obtained when the $(CH_3)_3NBBr_3$: BF_3 mole ratio was 1 : 10. Under identical conditions it was also found that $(CH_3)_3NBCl_3$ would react with BF_3. Thus the boron trichloride complex does react with a weaker Lewis acid and an equilibrium is probably established.

To examine more closely the possibility that preionization may play a predominant role in halogen exchange, samples of adducts in an ionic environment were prepared. Both halogen hydrides and tetraalkylammonium salts were used for this purpose. The results almost universally showed that no reaction occurred. This may be taken as good evidence against a facile rupture of the boron halogen bond. The most probable mechanism for halogen exchange to occur may thus involve the halogen bridged intermediate. The notable exception was $(CH_3)_3NBI_3$. This adduct reacted fairly readily with BF_4^-, BCl_4^-, Cl^- and Br^- to form mixed adducts, except in the F/I system. Surprising was the apparent lack of reaction with BBr_4^- which is not easily

explained at present. It is possible that the reaction products were obscured by the large n-butyl proton resonance. Halogen exchange occurred more easily when $(CH_3)_3NBI_3$ was mixed with HBr in the presence of a trace of water compared with the anhydrous system. Water therefore seems to play an important role in the exchange reaction of $(CH_3)_3NBI_3$ with HBr, presumably by encouraging the ionization of the latter.

The mechanism of acid and alkali catalysed hydrolysis of $(CH_3)_3NBF_3$ (192) and $(CH_3)_3NBCl_3$ (193, 196) has been studied. For $(CH_3)_3NBF_3$, an S_N1 dissociation of the coordinate bond is the rate determining step, while for $(CH_3)_3NBCl_3$, S_N2 attack of water and rupture of the B-Cl bond probably controls the rate. Decomposition products were noticed during this work, but their study was not pursued.

It is worth noting that one of the mixed adducts, namely $(CH_3)_3NBX_2I$ was normally discriminated against. Its concentration was considerably lower than other adducts in the reaction mixture. The ability of iodine to behave as a leaving group may be enhanced in the monoiododihalogenoborane complexes. This evidence supports, for this system, the ionic first order dissociative mechanism of Krishnamurthy and Lappert (241), particularly since isotopic labelling again showed that the dative bond remained intact.

The reaction then may proceed through the following mechanism:-

$$(CH_3)_3NBI_3 \longrightarrow [(CH_3)_3NBI_2]^+ + I^- \qquad 13.$$

$$[(CH_3)_3NBI_2]^+ + Cl^- \longrightarrow (CH_3)_3NBI_2Cl \qquad 14.$$

Solution reactions of adducts with adducts supplied further evidence to help rule out the possibility of B-N bond cleavage under moderate conditions. The results showed that no halogen exchange occurred when two adducts were mixed in solution and maintained, for several months, at 50°C. This supports previous work (239) in which a solution of $(CH_3)_3NBF_3$ and $(CH_3)_3NBCl_3$ was heated to 180°C in an unsuccessful attempt to prepare mixed adducts. If the coordinate bond did rupture during these reactions, free boron trihalide would be generated and mixed adducts could be expected.

These results contrast sharply with information from the dimethyl ether-BX_3 system (238). Halogen exchange occurs apparently because the weaker B-O bond is constantly breaking and reforming; thus a small concentration of trigonal boron trihalide is present in solution.

At higher temperatures however, and in the absence of a solvent, dissociation of the coordinate bond does become an important factor in halogen exchange reactions.

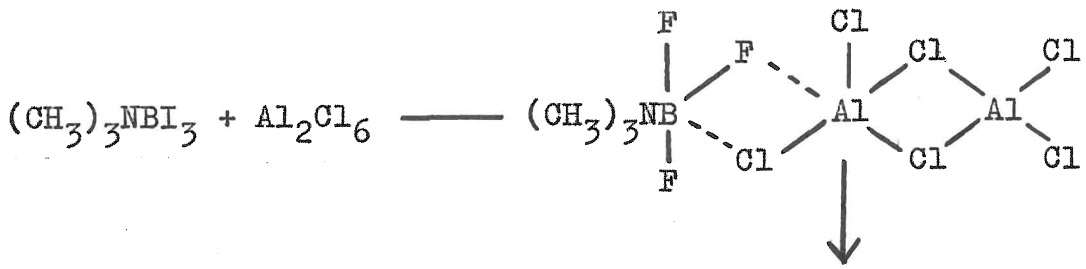
This was first suggested by Coyle (186) who used $Et_3N^{10}BF_3$ as an aid in an investigation of that adducts reaction with BCl_3. He found that at 60°C, reaction occurred via a B-N bond breaking mechanism since almost complete isotopic equilibration was noted; at 0°C, only 5% of the boron had exchanged indicating that a different reaction pathway was operative. These results substantiated his findings. Initial attempts at reacting adducts at 300°C resulted in too much decomposition to allow satisfactory conclusions to be drawn. Accordingly the temperature was lowered to 160°C. Reaction between two adducts did not provide any meaningful data even when one adduct was enriched in boron-10. In this case either of the mechanisms, dissociative or concerted, would provide mixed adducts containing both isotopes of boron. Admittedly, a very crowded transition would tend to preclude the concerted mechanism. If, however, an adduct containing only boron-10 was allowed to react with a free boron trihalide -- containing natural abundance boron -- the mechanism would be established if the mixed adducts contained boron-11. The results of this work clearly showed that isotopic equilibration had occurred. Thus dissociation of the B-N bond must be the operative mechanism. The free boron trihalides would undergo halogen scrambling and recomplex when the mixture was cooled. The reactions may be summarised thus:-

$$(CH_3)_3N^{10}BY_3 \xrightarrow[\text{gas phase}]{160^\circ} (CH_3)_3N + {}^{10}BY_3 \qquad 15.$$

$${}^{10}BY_3 + BX_3 \rightleftharpoons {}^{10}BY_2X + BX_2Y \qquad 16.$$

$$\left.\begin{aligned} {}^{10}BY_2X + (CH_3)_3N &\longrightarrow (CH_3)_3N{}^{10}BY_2X \\ BX_2Y + (CH_3)_3N &\longrightarrow (CH_3)_3NBX_2Y \end{aligned}\right] \qquad 17.$$

The results of the reactions of the trihalide adducts with the anhydrous metal chlorides are difficult to interpret. Aluminium chloride can behave as a Lewis acid. Because of its proximity to boron it seems reasonable to expect that it would react fairly readily at ambient temperatures. Aluminium chloride is normally a dimer; little or no evidence supports the existence of monomers, particularly in a relatively non-polar solvent such as methylene chloride. If monomers did exist in solution, a bridging exchange mechanism similar to that mentioned above (equation 3) could be suggested. This may still be the case although considerable steric hindrance would be expected in the transition state.



The possibility of B-N bond rupture cannot be ruled out either. Less likely is an ionic mechanism in which pre-ionization of the boron-halogen bond occurs. The reluctance of adducts, except $(CH_3)_3NBI_3$, to react with ionic species has already been noted. Pre-ionization may be a contributing mechanism to the interaction of the latter adduct with Al_2Cl_6 and the lack of $(CH_3)_3NBCl_2I$ in the systems $(CH_3)_3NBI_3/SiCl_4$ and $(CH_3)_3NBI_3/AsCl_3$ may indicate that it dominates these reactions too; particularly since analogous exchange in the BF_3 and BBr_3 adduct samples was not observed.

The reaction of adducts with PCl_5 supplies some interesting data. $(CH_3)_3NBF_3$ and $(CH_3)_3NBI_3$ were observed to undergo halogen exchange; $(CH_3)_3NBBr_3$ did not react. An S_N1 mechanism may be ruled out because previous results indicate that rupture of the B-N bond does not occur under mild conditions in solution. If a bimolecular S_N2 mechanism controlled the reaction, the transition state complex would be very crowded. The considerable steric strain expected for such a complex may well preclude its formation. The reaction may proceed via a polar mechanism in which PCl_5 would abstract a fluorine atom from the adduct and form a hexacoordinate ion. Formation of a boron-chlorine bond during further interaction of the PCl_5F^- ion with the $\left[(CH_3)_3NBF_2\right]^+$ unit would yield the neutral chlorinated

adduct. This polar mechanism could also explain why $(CH_3)_3NBBr_3$ does not react with PCl_5. The bulky bromine atom may prevent the formation of PCl_5Br^-, even though B-Br bonds in the adducts are more easily broken than B-F bonds. This suggestion could be tested by mixing $(CH_3)_3NBF_2Br$ or $(CH_3)_3NBFBr_2$ with PCl_5. If the mechanism is valid, formation of $(CH_3)_3NBCl_2Br$ and $(CH_3)_3NBClBr_2$ respectively, would be expected. The tertiary mixed adduct, $(CH_3)_3NBFClBr$ may also be formed. Again, for $(CH_3)_3NBI_3$, a mechanism involving pre-ionization of the B-I bond may be the best explanation, particularly since the mixed adducts are discriminated against.

Halogenation of TMAB

TMAB reacts readily with HX (X = Cl, Br and I) to form $(CH_3)_3NBH_2X$. A large excess of HX does not force the reaction further forward to any great extent. Stronger reagents, particularly chlorinating compounds, have allowed the preparation of the dihalo- and trihaloborane adducts (156, 171, 173). Two possible mechanisms of halogenation, presented by other workers (156, 173), have been discussed in the introduction of this work, Chapter I, Section C(i). One involves a concerted transfer of a halogen atom to the adduct as it loses a borane proton; the other operates via a free radical chain reaction. Recent work by

Ryschkewitsch and Miller (277) not only supports a free radical mechanism, but also shows that a polar reaction pathway is possible under certain conditions. Their evidence for a chain reaction is based on the reaction of amine boranes with the alkyl halides 1, 2- $C_2H_4Cl_2$, CCl_4 and CCl_3Br. The results indicate that the reactions proceed considerably faster in the presence of benzoyl peroxide -- a free radical initiator -- to produce the same products in the same proportions. They conclude that this invariance of product distribution arises because both reactions (the uninitiated and peroxide-initiated reactions) proceed through the same path. Polar reactions were observed with organic halides which readily formed carbonium ions. Thus chlorotriphenylmethane reacts with 4-methylpyridine borane in the following manner:

$$4\text{-Mepy.}BH_3 + (C_6H_5)_3C^+Cl^- \longrightarrow (C_6H_5)_3CH + 4\text{-Mepy.}BH_2^+ + Cl^- \qquad 19.$$

$$4\text{-Mepy.}BH_2^+ + Cl^- \longrightarrow 4\text{-Mepy.}BH_2Cl \qquad 20.$$

The stable carbonium ion abstracts a proton from the borane entity; the boronium ion then bonds to the chloride ion to yield the chlorinated adduct. That the rate of these reactions was found to depend on the stability of both the carbonium and boronium ions formed, is good evidence to support the polar mechanism.

A concerted mechanism, similar to that proposed earlier (156), may be the best explanation of the reaction between TMAB and HX (X = Cl, Br, I). The lack of any species that could abstract a borane proton from the adduct, and the observation that a trace of water inhibits the reaction, may rule out the polar mechanism. A free radical pathway cannot be eliminated entirely.

It has been suggested (55) that trace impurities may be responsible for initiation of a radical chain that allows CCl_4 to react with amine boranes. A similar argument could be invoked here. However, the hydrogen halides were purified before use and the reaction was fast. Such observations render a free radical mechanism less likely. When the reaction of TMAB with bromine and iodine is considered, a chain reaction seems plausible and is probably the best explanation.

Interesting observations were recorded after TMAB had been allowed to react with free trihalides and other adducts at 120°C in the gas phase. In the systems $TMAB/BX_3$ (X = Cl, Br, I) mixed adducts were formed in reasonable quantities. When two adducts, $TMAB/(CH_3)_3NBX_3$ (X = Cl, Br) were mixed, only traces of mixed adduct were detected. When $(CH_3)_3NBI_3$ and TMAB were mixed and heated, only mixed adducts were present.

These observations may be explained by suggesting

that at 120°C very little dative bond cleavage is occurring in TMAB. This could easily be checked by using boron-10 labelled adducts and would have been carried out had time allowed. Free BX_3 would then attack TMAB via the concerted mechanism to form mixed adducts. The trace of mixed adducts in the TMAB/adduct systems may be explained in two ways. Firstly, the temperature may be too low to allow the reaction to proceed to any great extent. Secondly, if the dative bond rupture is negligible, exchange may be limited to an S_N2 mechanism between two adducts. This transition state would be sterically hindered. An alternative explanation has to be sought for the system with $(CH_3)_3NBI_3$ and TMAB in which exchange was readily achieved. It is possible that the B-I bond is breaking and that the free iodine attacks TMAB. If this was the case a purple colour could surely be expected; yet it was not detected. $(CH_3)_3NBI_3$ is not known to vapourize -- it will not sublime at 300°C. Diborane may therefore attack the triiodide adduct, reaction being facilitated because the B-I bonds can be relatively easily heterolysed. The results of these reactions are far from conclusive and it is obvious that this interesting area offers good possibilities for future studies.

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